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Textile dyeing in Mali
Possibilities for small scale effluent treatment

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Textile dyeing in Mali - possibilities for small scale effluent treatment

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Cover: Women washing dyed fabric in the Niger River in Bamako, Mali
Photo: Hanna Larsson

Abstract

Water treatment is an important issue in Mali, an arid country where the Niger River is the main recipient for a large part of the effluents from industrial and small scale activities. Clothes dyed with synthetic dyestuffs are an important part of the culture in Mali. Dyeing of textiles is to a large extent an informal activity, mainly performed by women.

The objective for this thesis work was to investigate potential capacity of cheap, locally accessible materials in treatment of effluents from textile dyeing. Effluents studied were sampled at three sites with small scale textile dyeing in Bamako, Mali. At two sites the effluents were emitted directly to the Niger River, at the third site the effluents were collected in a soakaway. The capacity of different materials, both coagulants and adsorbents, to treat the effluents was analysed with jar tests. pH, conductivity, total dissolved solids (TDS), turbidity and dissolved oxygen (DO) were analysed on samples before and after jar tests, and on river water from spilling site. For some jar tests, UV-Vis spectra and content of zinc, nickel and copper were analysed. Properties of dyestuffs were analysed with spectrophotometry, scanning electron microscopy (SEM) and nuclear magnetic resonance spectroscopy (NMR).

Iron(III) chloride coagulated dye effluents, efficiently removing most of the colour from water. Activated carbon, both in granulated form and in the form of powder, showed some capacity to adsorb compounds in dye effluents. Rice chaff, rice bran, laterite, bentonite and aluminium sulfate did not show capacity to remove dyes from effluents.

The composition of the dyestuffs used in small scale dyeing is not known, which is a serious problem when developing treatment methods. A significant fraction of the dyestuffs consists of substances which are not part of the colour-yielding dye. Five dyestuffs with different colours were analysed with SEM with X-ray fluorescence detector. These dyestuffs contained, except for carbon, oxygen and nitrogen which can not be detected, mainly sulfur, chloride, sodium and, in the case of green, barium. Traces of chromium, vanadium, iron, aluminium and silicon were also detected in some of the dyestuffs. Mixed effluents from two sampling sites contained concentrations of zinc and nickel higher than WHO guideline values for drinking water.

Further studies are needed to find a cheap treatment method since low cost materials such as rice bran and laterite are ineffective. In addition to be able to remove polluting substances from dye effluents, the method should include cheap and readily accessible materials, and be supported by an infra-structure which allows the effluents to be treated locally. To find a working solution to decrease water pollution, without threatening the livelihood for dyers, co-operation between universities, dyers and governmental bodies is crucial.

Keywords: Water treatment, textile dyes, artisanal, Mali.

Resumé

Le traitement des eaux usées est important au Mali, un pays largement sec où le fleuve Niger est récepteur de la majorié des effluents industriels et artisanals. Le fleuve est aussi une source d'eau potable et est important pour la pêche locale.

L'histoire de teinture est longue en Afrique de l'Ouest, à l'époque effectuée avec des materiaux naturels, mais à parti des années 1950 de plus en plus avec des colorants synthétiques. Les tissus en cotton tissés avec la technique damas et colorés par des colorants synthétiques, appellés basins, sont importants dans la culture Malienne. Ils sont utilisés pour des vêtements portés pendant des cérémonies mais aussi dans la vie quotidienne. À Bamako, la teinture des textiles est effectuée principalement par des femmes dans un secteur informel avec des méthodes artisanales.

L'objectif de ce travail était d'étudier la possibilité de traiter des effluents de teinture de textile artisanal à Bamako avec des materiaux locaux pas chers. Les échantillons des effluents ont été pris dans trois sites de teinture artisanal à Bamako. Les effluents étaient déversés en direct dans le fleuve Niger dans deux sites, tandis que dans le troisième site les effluents sont déversés dans un puisard. Ensuite, des échantillons de l'eau du fleuve aval et de l'eau du fleuve où les effluents sont déversés, ont été pris.

Le pH, la conductivité, le TDS, la turbidité et l'oxygène dissous sont analysés pour les effluents brut et les échantillons de l'eau du fleuve. La capacité des differents materiaux de traiter les effluents a été analysé avec des jar tests. Les materiaux ajoutés étaient la bentonite, le charbon activé en poudre et comme granules, laterite en poudre, son de riz en poudre et balle de riz. Ensuite, des solutions de sulfate d'aluminium et de chlorure de fer(III) étaient utilisées. Le pH, la conductivité, le TDS, la turbidité et l'oxygène dissous sont analysées avant et après jar test. Pour quelques jar tests des spectres UV-Vis et le contenu des metaux zinc, nickel et cuivre sont analysés. Les propriétés des colorants sont analysées avec spectophotométrie, microscope électronique et résonance magnétique nucléaire.

Le chlorure de fer(III) a coagulé les effluents de colorants, c'est à dire les particules polluantes ont formé des flocs et sont sédimentés, laissant l'eau séparée des polluants. Le pH était baissé de 13 jusqu'à 2. Le charbon activé, en poudre et granulé, a montré la capacité d'adsorber les molecules qui absorbent les radiations électromagnetiques dans l'interval UV et visible, de la solution d'effluent. Bentonite, laterite, son de riz, balle de riz et sulfate d'aluminium n'ont pas séparé les polluants de l'eau.

Le développement d'une méthode de traitement est limité par le manque de données sur la composition chimique des colorants utilisés. Une fraction importante des colorants vendus est composée d'autres components que la substance qui donne la couleur. Les cinq colorants analysés (vert, jaune, rouge, bleu et violet) sont solubles dans l'eau distillée, 0,01 M acide nitrique et 0,01 M hydroxide de sodium, et avaient la même couleur dissous dans les trois solvants. L'analyse avec microscopie électronique et un detecteur de fluorescence des rayons X a montré que les colorants sont composés de soufre, chlore et sodium, outre de charbon, oxygène, hydrogène et azote qui ne sont pas détectés avec cette analyse. Pour le colorant vert, une concentration de barium relativement élevée a été détecté. Des traces de chrome, vanadium, fer, aluminium et cilisium ont aussi été détectées.

La recherche pour trouver une méthode de traitement des eaux usées de la teinture artisanalle à Bamako doit continuer car ce travail n'a pas trouvé de solution. Le materiel utilisé devrait séparer les polluants de l'eau et ne pas être cher. Ensuite une infrastructure pour le traitement est necessaire. Une cooperation entre l'université, les teinturières et les autorités est importante pour trouver une solution qui diminue la pollution de l'eau sans menacer l'entretien des teinturières.

Mots clés: Traitement de l'eau, teinture de textile, artisanal, Mali.

Sammanfattning

Textilfärgning har en lång tradition i Västafrika. Ursprungligen användes olika växtmaterial, men sedan 1950-talet har syntetiska färgämnen kommit att användas i allt större utsträckning. I Bamako, huvudstad i Mali, är färgglada kläder ett vanligt inslag i gatubilden, i synnerhet på fredagar, då muslimernas stora bön hålls, och på söndagar, då många bröllop firas. Textilfärgningen är också en viktig inkomstkälla för många i Bamako. Antalet som färgar är inte känt eftersom det är en informell sektor utan någon form av registrering, men i en av stadens sex kommuner beräknas omkring 300 textilfärgningsenheter finnas. Det är främst kvinnor som färgar, medan männen knyter mönster på de vita tygerna före färgning och slår de färgade tygerna med träklubbor för att göra dem glänsande och pappersaktiga vilket önskas av kunderna.

Färgningen utförs i metallkärl som värms upp genom vedeldning. Tygerna doppas för hand i färgbadet och sköljs därefter, i många fall direkt i Nigerfloden som rinner genom staden. I vissa fall används handskar av de som färgar, och i undantagsfall andningsskydd mot ångor från färgbaden, men de flesta har direktkontakt med färglösningen. Utsläppen av använda färgbad sker antingen direkt till floden eller till avloppskanaler som så småningom leder ut i floden. Ett fåtal enheter har någon form av uppsamling av utsläppen. Dessa utsläpp av färger bidrar till att försämra kvaliteten på yt- och grundvatten i Mali. Dessutom påverkas även andra länder, eftersom föroreningar transporteras nedströms floden. Nigerfloden har sitt ursprung i Guineas bergstrakter, passerar Bamako och fortsätter genom Mali, Niger och Nigeria innan den når havet i Guineabukten. Vattenkvaliteten i floden är därför en gränsöverskridande fråga, och det är viktigt att varje land arbetar för att minska sina utsläpp för att undvika framtida konflikter kring vattenkvalitet. Det är dessutom viktigt för Mali som land att på ett bra sätt förvalta sina vattenresurser, eftersom en stor del av landet har ett mycket torrt klimat.

Tillgång till rent vatten är viktigt för en god hälsa, och därmed för en hållbar utveckling och fattingdomsbekämpning. I dagsläget har bara hälften av Malis befolkning tillgång till någon sorts förbättrad vattenkälla. Minskning av utsläpp av skadliga ämnen till miljön är också viktigt för en hållbar utveckling, för att naturresurser skall kunna användas utan risk idag och i framtiden.

Syftet med denna uppsats var att undersöka om det finns billiga material, tillgängliga i Mali, som kan användas för att rena utsläpp från småskalig textilfärgning. Prover från textilfärgsutsläpp insamlades på tre olika platser i Bamako, två belägna vid Nigerflodens strand och en i ett bostadsområde relativt långt från floden. På de två förstnämnda platserna arbetar relativt många kvinnor med färgning och färgbaden töms direkt i floden, där även de färgade tygerna sköljs. Verksamheten i bostadsområden drivs av tre kvinnor i en familj och här töms använda färgbad i en avloppsbrunn. Två viktiga problem i arbetet för att övervaka och rena utsläppen från den hantverksmässiga textilfärgningen är dels att det finns mycket lite information om vattenkvaliteten i Nigerfloden och hur den har förändrats, dels att färgämnena som används är okända eftersom de säljs i plastpåsar utan innehållsförteckning.

De material som användes i försök att rena utsläppen var lågkostnadsmaterialen risskal, risagnar samt laterit. Laterit bildas i tropiska områden genom lång tids vittring på ytan av berggrunden och består av kaolinit, kvarts och järnoxider. Dessutom undersöktes bentonit och aktivt kol, både i pulverform och som granuler, samt aluminiumsulfat och järn(III)klorid vilket är ämnen som används i konventionell vattenrening. Materialen tillsattes till bägare med färgutsläpp, blandningen rördes om under 1,5 timmar och kemiska parametrar mättes före och efter detta så kallade *jar test* för att se om behandlingen hade någon effekt. Dessutom analyserades kemiska egenskaper hos fem färgämnen som används för textilfärgning i Bamako.

Järn(III)klorid fungerade bäst för att separera färgutsläpp från vatten, men gav ett mycket lågt pH-värde och en gul-brun färg på vattnet. Aktivt kol visade viss förmåga att adsorbera föroreningar, i synnerhet kol i pulverform, men gav ingen synlig minskning av provernas färgkoncentration. Risagnar och risskal, bentonit, laterit samt aluminiumsulfat hade ingen renande effekt på textilfärg-

sutsläppen i undersökningen.

Grönt, gult, rött, blått och violett färgämne innehöll enligt analys med elektronmikroskop utrustat med röntgenfluorescensdetektor förutom kol, syre och kväve som inte kan detekteras, till störst del grundämnena svavel, natrium och klor. Det gröna färgämnet innehöll även relativt mycket barium. Spår av krom, vanadin, järn, aluminium och kisel hittades också i de olika färgämnena. En stor del av färgpulver som säljs består ofta av tillsatsämnen utöver den förening som ger färg. Analys av det gröna färgämnet visar att den gröna färgen sannolikt kommer från en aromatisk molekyl.

Slutsatser från detta arbete är att större kunskap om färgämnenas kemi krävs för att hitta en fungerande reningsmetod. Frågan är dock komplex och rör inte enbart kemi. Om en kemiskt fungerande metod med billiga, tillgängliga material hittas, måste en infrastruktur där reningen kan ske byggas. Detta är i många fall en investering som inte är ekonomiskt möjlig för kvinnorna som färgar. För att hitta en fungerande lösning för rening av textilfärgsutsläpp i Mali krävs samverkan mellan universitet, de som färgar, lagstiftare samt myndigheter med ansvar för tillämpning av lagar.

Nyckelord: Vattenrening, textilfärger, hantverksmässig verksamhet, Mali.

Filthy water cannot be washed

African proverb

Life shrinks or expands in proportion to one's courage

Anais Nin

Badalabougou, Bamako

Mariage à Bamako

Batême à Selingué

PREFACE

Le dimanche à Bamako c'est le jour de mariage
Les hommes et les femmes ont mis leurs beaux boubous /.../
Les bazins et les bogolans sont au rendez-vous /.../
Le dimanche à Bamako c'est le jour de mariage.

Sunday in Bamako is the day for weddings
Men and women wear their beautiful boubous /.../
Bazin and bogolan meet /.../
Sunday in Bamako is the day for weddings.

Amadou & Mariam
Beaux Dimanches
Dimanche à Bamako 2005

Bamako is a city full of colour. Mariam and Amadou describes the Sundays in Bamako, the day for weddings, and they do not leave out the cloths, the *boubous* in bright coloured *bazin* which makes any wedding party a symphony of colours. Also on Fridays, the day for *jumu'ah*, the great prayer for muslims, the streets are more coloured than usual by beautiful tissues. Clothes in western style are used, but the habit to wear brightly colored bazins even in everyday life is well established in Bamako.

However, the production of these beautiful clothes has negative consequences for the environment. Residual colour baths containing colorants and auxiliaries are emitted to the Niger River, to slurry channels or to soakaways in housing areas without any treatment, causing transport of a substantial amount of unknown compounds to surface water and groundwater.

The water of the Niger River is used for many activities. Apart from beeing recipient for effluents from industrial and artisanal activities, it is also used for washing of clothes, cars and motorcycles. At the same time it is used for fishing and, after treatment, as drinking water for a large part of Bamako. This makes the water treatment issue important, but also complex.

I hope that you while reading this masters thesis not only learn something about the chemistry of dyestuffs and water treatment methods (if you are not already an expert in this field) but also get a feeling for the complexity of water and waste management issues in a low income country, and learn something about Mali, a country unknown to many Swedes.

I have learnt a lot during my three month stay in Bamako and I am grateful fo the possibility to see another reality through the Minor Field Study grant. Happily I left for something unknown! As one of my colleges in the lab wrote to me after my departure: "better seen [the limited resources but happiness and strong feeling of solidarity] than being told 100 times."

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Definitions

adsorption - accumulation of a dissolved substance on a solid surface through chemical bonds of different strength.

aquifer - geological formation containing groundwater.

Badala - "by the river" (Bam.).

Bambara - language spoken in Mali, abbreviated Bam.

Biological Oxygen Demand (BOD) - amount oxygen consumed during biological oxidation of organic matter in water. Often measured during five days, indicated with a subscript, BOD_5.

bituminous coal - the most abundant form of coal, intermediate in rank between sub-bituminous coal and anthracite according to the coal classification in USA and Canada.

Bougou - "city" or "built-up area" (Bam.).

cesspool - underground installation to collect wastewater.

Chemical Oxygen Demand (COD) - amount oxygen needed to oxidize organic matter present in water. Does not differentiate between biologically degradable and non-degradable compounds.

coagulation - destabilization of a colloidal suspension leading to aggregation of particles.

conductivity - capacity to conduct electric current; hence a parameter describing content of dissolved ions in water samples.

fault - a crack in the earth's surface where the rock has divided into two parts which move against each other.

flocculation - the physical process of producing interparticle contacts, flocculants are used to increase the strength of flocks formed through coagulation in water treatment.

Internal Renewable Water Resources (IRWR) - ground water and surface water generated from endogenous precipitation in a country. It does not count deep aquifers that have a neglible recharge in a human time-scale, as these are considered non-renewable.

lignite coal - the first result of coalification of peat. It is classed as intermediate between peat and sub-bituminous coal in the coal classification used in USA and Canada

soakaway - underground installation to collect waste water.

Total Dissolved Solids (TDS) - content of organic and inorganic substances present as molecules, ions or colloids in a solution.

turbidity - a measure of the degree to which water loses its transparency due to presence of suspended particles.

List of abbreviations

BOD - Biological Oxygen Demand

COD - Chemical Oxygen Demand

DE_T - dye effluent from Torokorobougou

DE_B - dye effluent from Badalabougou

DE_O - dye effluent from Ouolofobougou

DO - Dissolved Oxygen

FTU - Formazine Turbidity Unit

GAC - Granulated Activated Carbon

IRWR - Internal Renewable Water Resources

MFS - Minor Field Study

NMR - Nuclear Magnetic Resonance

PAC - Powdered Activated Carbon

PRSP - Poverty Reduction Strategy Paper

rpm - revolutions per minute

SEM - Scanning Electron Microscopy

SIDA - Swedish International Development cooperation Agency

SS - Suspended Solids

TDS - Total Dissolved Solids

UNDP - United Nations Development Program

UNEP - United Nations Environment Program

UNESCO - United Nations Educational, Scientific and Cultural Organisation

USEPA - United States Environmental Protection Agency

USHHS - United States Department of Health and Human Services

1 Introduction

Access to clean water is one of the most critical issues for global health and development. According to the United Nations Development Program, 2.6 billion people lack access to clean water (UNDP, 2006). Around 40 developing countries provide clean water for less than 70 % of the population. One of these countries is Mali, where only 50 % of the population used an improved water source in 2004 (UNDP, 2007). Insufficient access to drinking water is one of a number of reasons stated why the morbidity and mortality is so high in Mali (UNESCO, 2006).

A wide range of factors affect the availability of clean water, including pollution, treatment of polluted water, water infra-structure and political decisions concerning distribution of water. Decreased effluents of polluting agents to water bodies is not only a question of political decisions and implementation of policy, but is also closely connected to culture and socio-economic factors. In this context, development of cheap treatment methods that are possible to implement in small scale activities is important to decrease negative impact on water quality, environment and health.

Access to clean water that can be used and consumed without risk for acute or long-term impact on health and environment is important for a sustainable development and poverty reduction. Protection and sustainable management of natural resources is one of 14 priority areas in the second generation Poverty Reduction Strategy Paper (PRSP) for Mali established for the years 2007-2011 (République du Mali, 2006). In this plan, creation of stations for treatment of liquid, solid and gaseous waste from industrial and handicraft plants in major towns is mentioned as a concrete example of actions needed. Finding a method to treat liquid waste from an important handicraft activity, textile dyeing, is one step to implement this plan.

The consequence of water availability and pollution is further acknowledged as listed as one of the three most important environmental issues in Mali by the United Nations Environment Programme (UNEP, 2008).

The main objective for this Master Thesis work was to investigate potential of cheap and readily accessible materials to treat artisanal textile dying effluents. The work also aimed to investigate chemical composition of the dyes used, and performance in dye removal of some materials used in conventional water treatment, to increase the knowledge that could facilitate fulfilment of the main objective.

1.1 Water situation in Mali

Mali is situated in the inland of West Africa and covers an area of 1,241,000 km^2, almost three times as large as Sweden. It borders Mauritania, Algeria, Niger, Burkina Faso, Côte d'Ivoire, Guinea and Senegal (Fig. 1). Bamako, the capital of Mali, is marked in red in Fig. 1.

1.1.1 Water resources

Two thirds of Mali is characterized as arid (UNESCO, 2006). The annual mean precipitation ranges from near 0 mm in the northern parts to about 1,500 mm in the southern parts of the country. 57 % of the country has a precipitation of less than 200 mm per year. Climate zones found in Mali are the *desert zone*, the *sahelian zone* and the *tropical zone with dry season* (Fig. 2). The Internal Renewable Water Resources (IRWR) in Mali as a mean value for the years 1977-2001 are relatively low (Table 1). With these dry natural conditions, sustainable management of water resources, including cheap and available wastewater treatment, is an important issue in Mali. Water supply, purification and regulation are threatened in all regions of Mali (UNEP/IISD, 2005).

1.1.1.1 The Niger River

The Niger River Basin is the second largest basin in Africa (Li et al., 2007) and the ninth largest river basin worldwide (Niger Basin Authority, 2001), draining 2 million km^2 in Algeria, Benin, Burkina

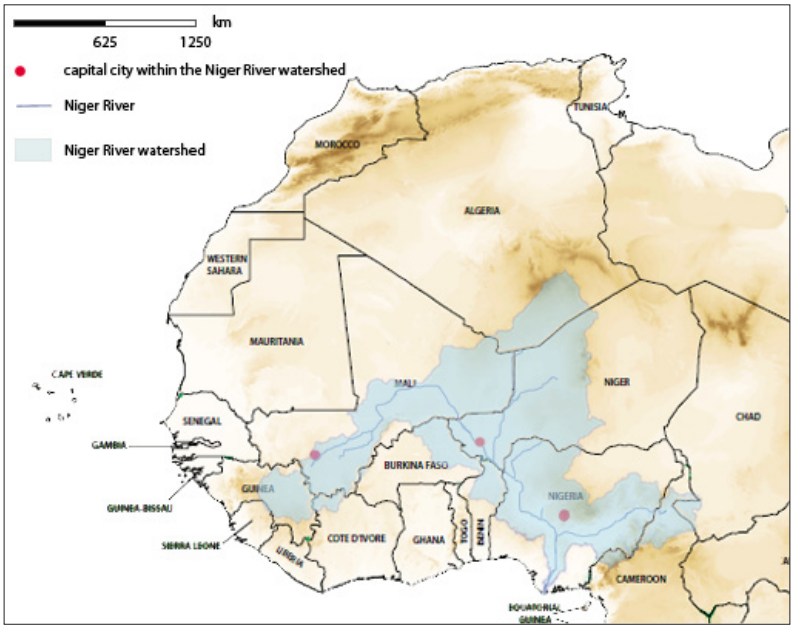


Figure 1. Political map of Western Africa. The transbondary Niger River watershed is marked in light blue. Modified from UNEP (2008) *Africa : Atlas of Our Changing Environment*. Division of Early Warning and Assessment, Nairobi.

Faso, Cameroon, Chad, Côte d'Ivoire, Guinea, Mali, Niger, Nigeria and Sierra Leone (Li et al., 2007; UNDP, 2006). The Niger River stretching 4,200 km from its headwaters in the Fouta Djallon massive in Guinea to its delta in Nigeria is the third-longest river in Africa (Olivry, 2005).

The transboundary basin of the Niger River is illustrated in Fig. 1. In such a large watershed, pollutants emitted in one area will affect water quality in the river downstream the effluent point. Bamako is situated quite far upstream the river, meaning that effluents from this city will affect surface water quality in a large part of Mali as well as in Niger and Nigeria. As seen in Fig. 1, effluents from three capital cities affect water quality in the lower parts of the Niger River; effluents from Bamako, Niamey and Abuja. The transboundary character of a watershed highlights the importance of international cooperation to avoid conflicts on responsibility for degradation of water quality. The degradation of water quality is a significant problem in the Niger River, where growth of larges cities on the river banks has not been accompanied by collection and treatment of waste water (Olivry, 2005).

Table 1. Internal renewable water resources in Mali, with comparisons to other areas.

	IRWR [m^3 $capita^{-1}$]	Reference
Mali	4,900	EarthTrends, 2003a
Subsaharan Africa	5,700	EarthTrends, 2003a
Europe	9,000	EarthTrends, 2003b
Sweden	19,300	EarthTrends, 2003b

1.1.1.2 Hydrogeology of Bamako city area

The hydrogeology of the Bamako city area can be characterized as two separate aquifers, one shallow and one deep (Orange & Palangié, 2006, Traoré et al., 2006). The shallow aquifer system consists of two different topographical areas: the lateritic hills of Koulouba with an highly fissured, highly permeable aquifer varying from 5 to 20 meters in depth, and the basin of the Niger River with an aquifer extending around the banks. Several important springs originate from the former,

while the latter is exploited through shallow wells and more influenced by water-level fluctuations.

The bedrock of consolidated sandstone is basically almost impermeable, but is a good aquifer due to fractures of different orientations caused by structural tectonic alteration (Traoré et al., 2006). This deeper aquifer is used as a drinking water resource for example in the suburban area where deep wells have been drilled.

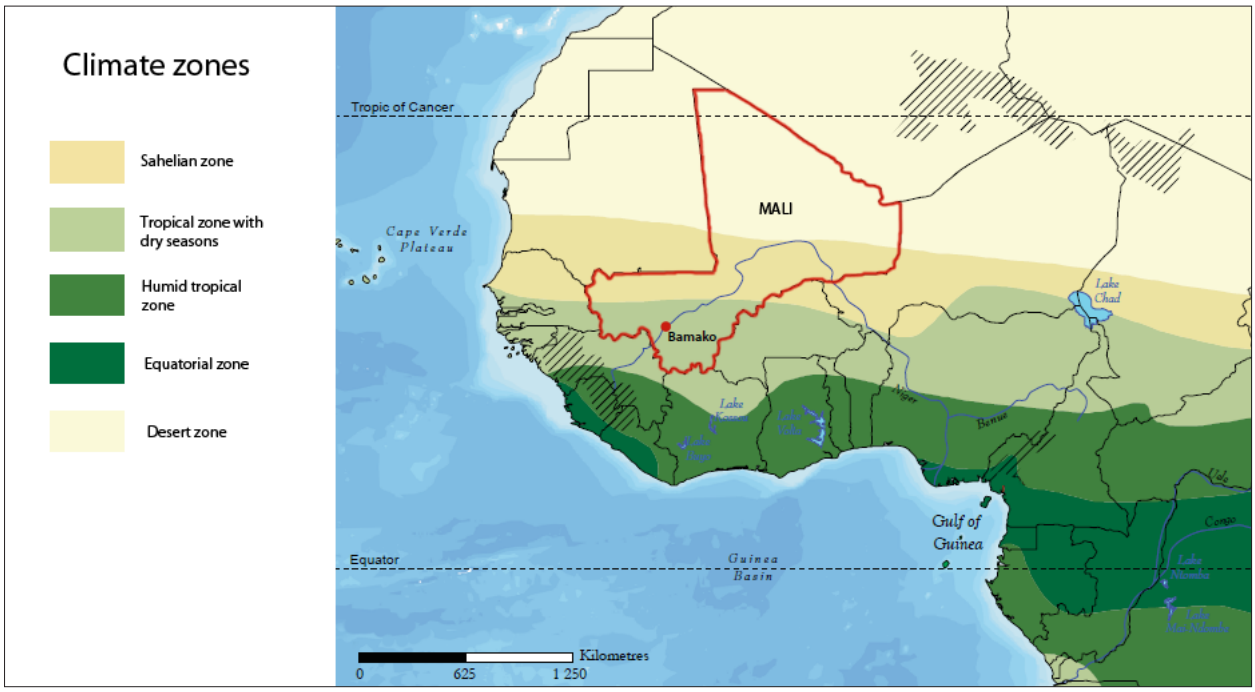


Figure 2. Climate zones in Western Africa. Modified from UNEP (2008) *Africa : Atlas of Our Changing Environment*. Division of Early Warning and Assessment, Nairobi.

1.1.2 Pollution of water resources

Knowledge of the water quality in Bamako is scarce; the Niger River is not systematically surveyed and there are no national guidelines for water quality (UNESCO, 2006). The focus in publications on water quality in Bamako is often, as for most developing countries, on drinking water quality, seldom on sanitation (Orange & Palangié, 2006). An even less investigated area is waste water quality and how to treat pollutants affecting water resources, knowledge which is important to develop efficient water purification processes. However, a few measurements have been made for some water quality parameters, showing an increase in nitrate and ammonia in the Niger River between 1980 and 1999 (UNESCO, 2006). Indicators of eutrophication and chemical pollution in the river is the high amount of vegetation and the cases of massive fish death, for example at the level of Magnambougou (Fig. 4) where a lot of artisanal activities takes place (Fofana, 2009) Deterioration of water quality in Bamako is closely connected to the large population growth of the city and the lack of a widely distributed sanitation system (UNESCO, 2006).

The ground water in Bamako is affected both by chemical and microbial polluting agents. The shallow aquifer is highly contaminated, e.g. with highly elevated concentrations of nitrate in relation to drinking water norms (UNESCO, 2006). This contamination can be explained by the high number of specific contamination sites in Bamako, the high permeability of the soil in certain areas and the high number of non-protected wells. In addition, the individual sanitation facilities present are not properly installed, which opens direct connections between surface and groundwater (Orange & Palangié, 2006). Sampling has shown influence of textile dye effluents from unsealed soakaways on water quality in wells in certain areas of Bamako, and the water was recommended not to be used for alimentation (Plea, 2009).

The water quality in the deep aquifer is still good, indicating that the transfer between the aquifers

is slow enough to prevent widespread pollution in the deeper aquifer. Limited downward migration due to higher hydraulic pressure in the semi-confined fractured sandstone aquifer is one explanation. However, drilling the deep aquifer might disturb this equilibrium and wells not sufficiently protected can be a direct pathway for pollution. The deep aquifer is directly connected to run-off waters in the fault to the east of the Bankoni cliff, an area currently used for dumping of waste materials among which car bodyworks and old batteries can be found.

Water quality varies during the year due to the seasonal climate. During the rainy season, run-off water carries a lot of organic material increasing biological oxygen demand (BOD), chemical oxygen demand (COD) and suspended solids (SS) in the Niger River (Orange & Palangié, 2006). On the other hand, concentrations of heavy metals are often lower during the rainy season due to dilution, indicating that run-off water does not carry high amounts of heavy metals. Climatic conditions are also a challenge for design of water treatment systems, as the load varies a lot over the year.

1.1.3 Water policy and legislation

The responsible governmental body for water quality issues in Mali is since April 2009 *Ministère de l'Energie et de l'Eau* (Ministery of Energy and Water), formerly *Ministère des Mines, de l'Energie et de l'Eau* (Ministery for Mines, Energy and Water) was responsible (Fofana, 2009). *Ministère de l'environnement et de l'Assainissement* (Ministery for Environment and Sanitation) and *Ministère de la Santé* (Ministery for Health) have also responsibility for questions related to the artisanal textile dyeing and the effluents of textile dyes to the river.

Several legislative and policy documents concerning water quality has been passed by the government, including *Code de l'Eau* (Law of Water Uses) 2002, *Politique national de l'eau* (National Water Policy) 2007, *Strategie Nationale d'Access en Eau Potable et Assainissement* (National Strategy for Access to Drinking Water and Sanitation) and *Plan de Gestion Integré des Resources en Eau* (Plan for Integrated Water Resources Management). An excerpt from the water law concerning the qualitative protection of waters is presented in Box 1.

Direction National de l'Assainissement et de Control de Pollution et Nuisances (National Direction for Sanitation and Pollution Control) is responsible for the implementation of the water policies. This is the youngest direction in Mali, created in 1998. What is written in the policy document is not coherent with what you see in reality. The weak implementation of water policy documents in Mali is not a question of funding, as the share for the sector in the budget has increased, but funds are not expended (Fofana, 2009). Fofana points out the lack of personnel as the main problem, both its quantity and its quality. Even corruption hinders implementation of water policy and control of polluting activities.

1.2 Textile dyeing

The common characteristic of all colorants is the ability to absorb visible light; electromagnetic radiation with wavelengths ranging from 400 to 700 nm. Where in this spectra the colorant absorb define its colour. Fig. 3 shows colours as a function of wavelength in the visible range. A compound with absorption peak in a certain interval of the spectrum will be perceived as having the complementary colour. Substances that are perceived as green have two absorption maxima; at 400-450 nm and at 580-700 nm (Zollinger, 1991). Absorption spectra for red, yellow, blue and purple are shown in Fig. 22.

Absorption of a dissolved chemical compound can be described with the Lambert-Beer law (Eq. 1), where I is the emerging intensity of radiation, I_0 the incident intensity of radiation, ε the molar absorption coefficient, c the concentration of species in the sample and l the path length of the radiation through the sample.

$$A = \log \frac{I_0}{I} = \varepsilon \, c \, l \qquad \text{Eq. 1}$$

Box 1. The Law of Water Uses. Cited and translated from République du Mali (2002).

Chapitre II: De la protection du domaine hydraulique
Section 1: De la protection qualitative

Article 14
Est interdit tout déversement ou écoulement, rejet, dépot direct ou indirect dans les eaux des matières de tout nature suseptibles de porter atteinte à la santé publique ainsi qu'à la faune et à la flore aquatiques. Toutefois, le ministre chargé de l'Environnement peut, après enquête publique et avis conformes des ministres chargés de l'Eau et de la Santé, autoriser et réglementer les déversements et écoulements visés à l'alinéa précédent dans le cas où ceux-ci pourraient être effectués dans les conditions garantissant l'absence de nuisance.

Article 15
Des normes de qualité des eaux peuvent être fixées par les autorités compétents de l'État dans certaines zones des cours d'eau jusqu'à la limite de salure des eaux. Des activités peuvent être réglementées ou interdites en fonction de ces normes de qualité.

Article 16
Toute personne physique ou morale, publique ou privée exerçant une activité, source de pollution ou pouvant présenter des dangers pour la ressource en eau et l'hygiène du milieu doit envisager toute mesure propre à enrayer ou prévenir le danger constaté ou présumé. Tout pollueur doit supporter les coûts de ses activités polluantes.

Article 17
Un arrêté conjoint des ministres chargés de l'Eau, de l'Environnement et de la Santé, détermine les mesures de prévention de la pollution et les conditions dans lesquelles sont effectués les contrôles des caractéristiques physiques, chimiques, biologiques et radiologiques des eaux.

Chapter II: The protection of the hydraulic domain
Section 1: The qualitative protection

Article 14
All direct or indirect discharge or efflux, disposal and dumping in waters of all kinds of matter likely to affect the public health or the aquatic fauna and flora is prohibited. However, the minister responsible for the environment can, after public inquest and complying advice from the ministers responsible for water and health, authorize and regulate the discharges or efflux approved for previous indenture in the cases where they can be carried out under conditions granting the absence of nuisance.

Article 15
Water quality norms up to polluted water can be fixed by the versed state authorities in certain zones of watercourses. Activities can be regulated or prohibited according to these quality norms.

Article 16
Any person, physical or juridical, public or private, performing an activity generating pollution or possibly threatening water resources and environmental hygiene should consider all appropriate measures to abate or prevent the observed or presumed danger.
All polluters should bear the costs of their polluting activities.

Article 17
A concerted decision of the ministers responsible for water, environment and health regulate the pollution prevention measures and the conditions under which the physical, chemical, biological and radiological quality controls of waters are executed.

Not only the position of the absorption peaks but also the intensity of the absorption band in relation to dye concentration is important for commercial dyeing (Zollinger, 1991). The intensity is described by the molar absorption coefficient ε in the Eq.1. Technical dyes have ε values ranging from 10^4 to more than 10^5 L mol^{-1} cm^{-1}. Dyes with high molar absorption coefficients are efficient, thus they give high colour intensity per mole dyestuff added.

All organic molecules used to colour textiles contain a chromophoric group, a conjugated system that can interact with light (European Commission, 2003). The first synthetic dyestuff, aniline, was explored in 1856 when William Henry Perkin worked with synthesis of a malaria medicine (Zollinger, 1991). This discovery stimulated chemists to perform similar experiments, and in the beginning of the 1860s the first true azo dyes were developed, nowadays the largest class of synthetic dyestuffs. Discoveries on the quadrivalence of carbon in 1858 and on the constitution

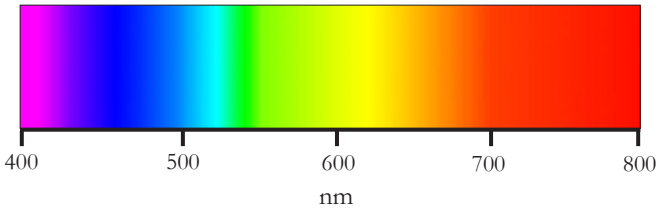


Figure 3. Colours as a function of wavelength in the visible spectrum of electromagnetic radiation.

of benzene in 1865 by August von Kekulé, enabled the preparation of synthetic dyes and artificial production of natural dyes. Since then several million coloured chemical compounds have been synthesised, of which about 10,000 on an industrial scale. Since the 1970s the research focus is more on optimization of manufacturing processes than on development of new coloured compounds.

Dyes can be distinguished from pigments as colorants applied to materials such as textiles from a liquid in which they are partly or completely soluble (Zollinger, 1991). Pigments are, on the other hand, pracically insoluble in the media in which they are applied and consist of particles that have to be attached to substrates by additional compounds such as polymers or plastics.

1.2.1 Classification of textile dyes

Textile dyes can either be classified according to their chemical structure or dependent on the chemical interaction between the dyestuff and the textile fibre. Based on the chemical structure, dyes can be grouped into polyene and polymethine dyes, di- and triarylmethine dyes and their aza analogues, aza[18]annulenes, nitro and nitroso dyes, azo dyes, carbonyl dyes and sulphur dyes (Zollinger, 1991).

The following section presents a classification of textile dyes based on interaction between dye and textile fibre, used e.g. by USEPA. Table 2 is a summary of what fibres different dye classes have affinity for and the typical percentage of dyestuff fixed to the fibers. There is also a column listing metals that are functional i.e. present in the structure of the dye molecule in some dyes in different classes. Metals can also be present in dye effluents deriving from impurities in dyes, fibers, salt and caustic soda (USEPA, 1996).

Table 2. Application and typical fixation rate for different dye classes. Typical metals in structure refers to metals typically included in the molecule of some dyes within the class (USEPA 1996).

Dye class	Fibers	Fixation (%)	Metals in structure
acid dyes	wool and nylon (polyamide)	80 - 93	copper, chromium and cobolt
azoic dyes	cotton and cellulose	90 - 95	
basic dyes	acrylic, certain polyesters	97 - 98	
direct dyes	cotton, rayon and other cellulosic	70 - 95	copper
disperse dyes	polyester, acetate and other synthetics	80 - 92	
fiber reactive dyes	cotton and other cellulosic, wool	50 - 80	copper and nickel
mordant (obsolete) dyes	pretreated natural fibers		chromium
sulfur dyes	cotton and other cellulosic fibers	60 - 70	
vat dyes	cotton and other cellulosic fibers	80 - 95	

1.2.1.1 Acid dyes

Acid dyes are water-soluble and have at least one sulfonic or carboxylic acid group in the molecule structure. The dyes are bound to basic amino groups in wool, silk and nylon fibers through ionic bonds with the sulfonic acid part of the dye molecule.

1.2.1.2 Azoic dyes

Azoic dyes are also known as naphthol dyes and consist of two compounds that react inside the fibers forming azo-chromophores. This dye class is mainly used on cotton but also on rayon, cellulose acetate, linen, jute, hemp and sometimes polyester.

1.2.1.3 Basic (Cationic) dyes

Basic dyes have limited water solubility, need addition of mordants for fixation and are applied in weakly acidic dyebaths. This group of dyes is rarely used on natural fibers.

1.2.1.4 Direct dyes

The name direct dyes can be derived from the fact that this group of dyestuffs can be applied to cellulosic fibers without mordants. Direct dyes are water-soluble, anionic compounds with a flat and narrow molecular structure allowing van der Waals forces and hydrogen bonds to form between dye molecules and fibers. Fixatives are generally used to increase color fastness. Sodium chloride or sodium sulfate is normally added in the dyeing process to counteract the slightly negative charge of cellulotic fibers in aqueous solution.

1.2.1.5 Disperse dyes

The water solubility of disperse dyes is very low and they are applied in form of a dispersion of finely ground powders in the dyebath. This group of dyes is mainly used for polyester and other synthethic fibers where the dyes are transfered into the fiber due to their higher affinity for this substrate.

1.2.1.6 Fiber reactive dyes

This group of dyes are water-soluble, anionic and form covalent bonds with the textile fibers, giving a high colour fastness. Fiber reactive dyes are mainly applied to cellulosic fibers such as cotton and rayon, but are sometimes even used for wool, silk and nylon dyeing. In general, large amounts of salts are added in the dyeing process and a high proportion of dye remain unfixed at the end of the process.

1.2.1.7 Mordant dyes

Mordant dyes usually contain a group acting as ligand forming coloured metal complexes with ions of aluminium, chromium, cobalt, copper, nickel or iron. These dyes are mainly used to colour wool but also silk and nylon.

1.2.1.8 Sulfur dyes

The synthesis of sulfur dyes includes a reaction at high temperature between nitro- and aminogroup containing organic molecules and sulfur or sodium sulfide. In the dyeing process, sulfur dyes are reduced with sodium sulfide forming a water-soluble compound with affinity for cellulosic fibers. When in contact with air after dyeing, the dye is reoxidized to its insoluble form, making this a group of dyes with good to excellent water fastness. Sulfur dyes are mainly used for dyeing cotton and rayon.

1.2.1.9 Vat dyes

Vat dyes are insoluble in water but soluble in alkaline solution. To make it migrate into the textile fiber, dyestuff is first reduced to its water soluble form, e.g. with sodium hydrosulfite. After dyeing the tissue is rinsed to remove surface colour, and the dye is reoxidized to its insoluble form within the fiber, giving a high water fastness. Vat dyes are mainly used to dye cotton and other cellulotic fibers.

1.2.2 Textile dyeing process

The dyeing method used by artisanal dyers in Bamako can be classified as a process that involve the diffusion of a dissolved or partly dissolved dye into the fibre, in contrast to pigment dyeing where an insoluble pigment is deposited on the textile surface and fixed with a binder, and to mass/gel dyeing where dyes are incorporated in synthetic fibers during their production.

The process of diffusion in to a fiber can from a molecular point of view be divided into four different steps (European Commission, 2003):

1. Diffusion of dye from dye solution to substrate.
2. Accumulation of dye on the textile surface, a process controlled by the affinity of the colourant for the fibre.
3. Diffusion of the dye to the interior of the fibre. This step is dependent on the accessibility of the fibre for the dye, which depends on if the fibre is hydrophilic or hydrophobic. Diffusion into micro-pores is limited by electrostatic forces on the surface of the fibres, which in some cases are reduced by addition of large amounts of salt in the dyeing process.
4. Fixation of dyes to the substrate through chemical binding. Dependent on dye used, this can involve covalent bonds, hydrogen bonds or van der Waals forces.

1.2.3 Environmental effects

The first visible effect of untreated effluents from textile dying is colour changes in the recipient. This is not only an aesthetic issue but can also disturb the photosynthesis and affect the aquatic life (European Commission, 2003).

Water polluting substances in effluents from textile dying can originate either from the dyes themselves or from other chemicals used in the dyeing process. These chemicals can be auxiliaries in the dye formulation, alkali, salts, reducing and oxidating agents and auxiliaries used in the dyeing process, or contaminants such as pesticide residues already present on the fibre when the dyeing starts (European Commission, 2003).

Effluents from textile and dyeing industry have been shown to cause toxic effects in several studies, but it is often difficult to isolate the specific compound causing a special toxic effect. Mathur et al. (2005) studied effluents from textile and dye industries in India and concluded that they contained highly mutagenic compounds and that dyes are probably responsible for the mutagenic activity. Houk (1992) compared in a review the mutagenicity in different industrial wastes and concluded the textile and dye industries to generate wastes and effluents of moderate mutagenicity.

1.2.4 Textile dyeing in Bamako

Textile dying has a long tradition in Western Africa, historically using natural colorants such as indigo from the tree *Indigofera arrecta*. Synthetic dyes arrived to the costal countries during the 1950s, and Malian dyers learned dyeing with the new colorants in Sierra Leone and Guinea during the 1960s (Gérimont, 2008). As synthetic dyes were easier to use, shortened the dyeing process and increased the number of colours possible to obtain, the traditional natural colours were gradually replaced. Since the beginning of the 1980s dyeing with synthetic dyestuff is widespread in Mali.

1.2.4.1 Textile dyeing today

In Bamako, industrial textile dying is mainly performed by two companies: Comatex. (Compagnie Malienne des Textiles) and Batexci (Bakary Textile Commerce et Industrie) both located by the Niger River (Fatou, in prep.). Effluent water from these plants are directed to the river after a simple filtration. However, the focus in this thesis is the large number of small scale textile dyeing units where the effluents are directed directly to the river or to streets, slurry channels or natural collectors, most often without any treatment. In some rare cases cesspools are used for treatment.

One important problem for the work to decrease the negative health and environmental effects of artisanal textile dyeing in Bamako is the lack of knowledge of the initial situation. As there is no

formal registration of dyers, their number is not known. The artisanal textile dyeing is estimated to emit more than 16,000 m^3 waste water each year (Diarra, 2006). The sector is informal and dyeing can be an activity performed by people excluded from the formal sector. Assistant dyers might be as young as 12 years old and their salary 10,000 Franc CFA (15 €) per month (Fofana, 2009). The working conditions depend on the employer, but many dyers work seven days per week without assurance, retirement benefits or holidays. The number of dyers in a part of Bamako has been investigated. In the fifth commune in Bamako (Fig. 4), about 300 textile dyeing units can be found (Fatou, in prep.). Two thirds of these emit the effluents to the streets, 15 % to slurry channels, almost 10 % directly to the river and about 10 % to a collector or a cesspool.

1.2.4.2 Origin of colorants

Neither the chemical composition of the dye stuffs nor the origin is indicated on the plastic bags in which they are sold to the dyers. However, trade statistics give an indication of the origin of dyestuffs. In 2006, 528 ton synthetic organic colorants were imported to Mali, of which half came from China, about a quarter from Côte d'Ivoire and between 5 and 10 % each from India, USA, France and the Netherlands (République du Mali, 2007). These numbers might not represent the actual inflow of colorants to Mali, as dyes are also sold on the black market imported via Guinea, Côte d'Ivoire, Nigeria and Senegal to avoid the customs fee (Fofana, 2009).

1.2.4.3 Dyeing process

Textile dyeing in Bamako is performed in the following main steps (Diarra, 2006): first the pattern is prepared on the cotton fabric. Thereafter the fabric is moistened in water and the desired dyes dissolved and heated to 55-70 °C. Sodium hydroxide is also added before the fabric is put in the dyeing solution. The fabric is agitated in the dye solution for about three minutes before it is washed in clean water. When all dye rests are washed away, the colored textile is washed with soap. At the end of the process the fabric is put in a starch solution to make it paper like and glistering before it is finally beat with wooden bludgeons to make it smooth and more glistering.

Dyestuffs used at the textile dyeing unit in Ouolofobougou (See Chapter 2.1.3) are from the beginning insoluble in water (Gérimont, 2008). Addition of sodium hydroxide and hydrosulfite changes the chemical properties of the dyestuff and makes it soluble in water. In this state it is possible for the dye to penetrate the fibers of the tissue. By washing the tissue in water after dyeing the dye is returned to its initial, insoluble state; hence fixed to the tissue. This process is described as a reduction/oxidation, but this is chemically implausible. Hydrosulfite is a reduction agent so reduction might take place, but reoxidation will not take place just through exposure to air. A possible reaction causing changes in dyestuff properties is deprotonation/protonation.

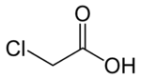
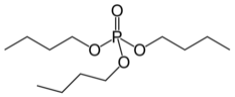
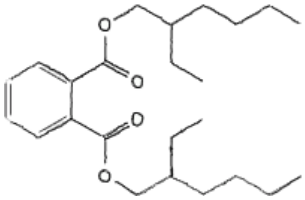
There are gender aspects of the work partitioning in the dyeing process. In general, attachment of ribbons to create the pattern is made by men, women perform the dyeing and men the final beating with bludgeons.

1.2.4.4 Chemical composition of dye effluents

The dyes used for textile dying in Bamako arrive in plastic bags without any indication of chemical composition. Table 3 is a list of compounds found in one investigation of textile dyes in Bamako, but other components that could not be detected by the equipment used could also be present (Lepinay, 2008).

In general, effluents from textile dyeing have high chemical oxygen demand (COD), a high concentration of suspended particles, very high pH, high concentrations of sulfate and in some colours heavy metals are present (Diarra, 2006). The starch used in the process is completely consumed and is not found in the effluents.

Table 3. Compounds found in a study of dyestuffs in Mali (Lepinay, 2008).

Compound	Formula
sodium chloride	NaCl
potassium hydroxide	KOH
chloroacetic acid	
tributylphosphate	
di(2-ethylhexyl)phtalate	
arsenic	As
metals	Cu, Zn, Cr, Ni, Pb, Cd, Hg.

1.3 Water treatment methods

This section will present some principles of water treatment and examples of plant materials and clays that have been used as low cost alternatives for water treatment in earlier studies. Finally the special chemical challenges for treatment of textile dye effluents are highlighted.

1.3.1 Coagulation and flocculation

Microorganisms and substances causing turbidity and colour in water are often present as colloidal particles, particles midway in size between dissolved compounds and suspended matter, with sizes ranging from 10^{-9} m to 10^{-5} m in diameter. Colloidal particles are stabilized (kept in suspension) by electrostatic repulsion between charged particle surfaces and by strong hydration. A colloidal suspension is destabilized by low surface charge, low hydration and impact of van der Waals forces. The process by which a colloidal suspension is destabilized and undergoes gravitational settling is called coagulation. In colloidal chemistry, *flocculation* is coagulation that produces bulky masses of settled particles with high water content, while *aggregation* is coagulation producing dense, organized masses of settled particles with low water content (Sposito, 1989). However, in the field of water treatment, the terminology is somewhat different. Here, *coagulation* refers to the reactions and mechanisms that result in particle aggregation, while *flocculation* refers to the physical process of producing interparticle contacts (Letterman et al., 1999). Sometimes, water treatment literature distinguish between *coagulants* and *flocculants*, where the former are used to destabilize the colloidal suspension and the latter are used to enhance floc formation and increase the strength of the floc structure.

1.3.1.1 Hydrolyzing metal salts as coagulants

The processes of coagulation, sedimentation and filtration are essential in many conventional water treatment systems to clarify the water and remove and inactivate viruses, bacteria and the cysts and oocysts of pathogenic protozoa (Letterman et al., 1999). Aluminum salts are by far the most widely used coagulants in water treatment (Ives & Al Azharia Jahn, 2002). Even iron salts are used to a wide extent and these have a broader pH-range for good coagulation, which makes them more suitable at low and high pH values in the water to be treated. These hydrolyzing metal salts have been used routinely since the beginning of the 20th century (Gregory & Duan, 2001).

The coagulating properties of these metal salts derives from the formation of specifically adsorbing counterions, ions with opposite charge to the colloidal particles, following addition of aluminium and iron salts to water solution. These counterions decreases or neutralizes the surface charge of the particles so that van der Waals forces can predominate causing destabilization of the system (Gregory & Duan, 2001).

1.3.1.2 Plant materials as coagulants

The coagulation and sedimentation processes have also been widely applied in small scale using biological materials as coagulants. Crushed seed material from the tree *Moringa oleifera* has traditionally been used as a natural coagulant to decrease turbidity of water in many African countries. More recent studies have shown that rest products from production of oil, which is used in production of food and soap, contains an active substance for water coagulation (Sutherland et al., 1994). Studies have been performed on the use of *M. oleifera* as a coagulant in water treatment (Ghebremichael, 2004) and as adsorbent for heavy metal removal (Sajidu, 2007).

In Tanzania seeds from *Vigna unguiculata*, *Parkinsonia aculeata* and *Voandzeia subterranea* are traditionally used to clear turbid water. The efficiency of extracts from these seeds as coagulants for water purification were studied by Marobhe (2008).

1.3.2 Adsorption

Adsorption can be defined as the accumulation of a substance at the interface between two phases (Snoeyink & Summers, 1999), in the case of water treatment between a liquid and a solid phase. The molecule adsorbed at the interface is called *adsorbate* and the solid at which the adsorption occurs is called *adsorbent*. The strength of the adsorbate-adsorbent interaction varies dependent on properties of the system. Two different groups of adsorption can be distinguished: *chemisorption* and *physical adsorption* (McBride, 1994). Chemisorption is characterized by strong interaction where covalent or short-range electrostatic bonds are formed between adsorbate and adsorbent, while physical adsorption involves less energetic adsorbate-adsorbent bonds.

The constant-temperature equilibrium relationship between amount adsorbate per unit adsorbent and the equilibrium solution concentration can be described with adsorption isotherms. This relationship depends on adsorbent characteristics such as surface area and pore size distribution. Adsorption is proportional to the available surface area within pores that are accessible to the adsorbate (Snoeyink & Summers, 1999). Further, adsorption is dependent on the affinity of the adsorbate for the adsorbent compared to its affinity for the solvent.

One example is the adsorption of organic molecules in water on activated carbon, an adsorbent widely used in conventional large scale water treatment. Increasing molecule size of adsorbate with addition of more hydrophobic groups will in general increase the adsorption to activated carbon from the water phase, as water solubility of the component is decreased. However, if molecules are approaching pore size, adsorption can decrease even though the water solubility of the molecule decreases. In this case increasing molecule size will decrease the diffusion rate within the activated carbon particles. Four different steps in the adsorption mechanism of organic molecules to activated carbon can be identified (McKay, 1982): Firstly, the molecules migrate from the bulk solution towards the surface of the adsorbent; secondly it diffuses through the boundary layer to the surface of the carbon. Thirdly, molecules are adsorbed at a site, but the process will also continue to the forth step where intraparticle diffusion transports molecules to the interior of the carbon. In this context, the carbon particle size is important. The rate of dye uptake increased with decreased mean diameter of carbon particles (McKay, 1982). Except for the effect of increased adsorption due to larger surface area for smaller particles, the internal diffusion path is longer in larger particles, increasing the probability for the molecule to encounter pores too small to enter.

1.3.2.1 Plant materials as adsorbents

Plant materials from many different species have been used as biosorbents in different water treatment studies. Soy meal hull was concluded to have suitable adsorption capacity to remove two red textile dyes from wastewater (Mahmoodi & Arami, 2008). Brazilian pine-fruit shell was used as a biosorbent to remove hydrolyzed and non-hydrolyzed reactive red dyes from aqueous solutions (Lima et al., 2008), and material from the algae *Ulva lactuca*, *Sargassum sp.* and *Cystoseira baccata* showed good adsorption capacity of methylene blue (Tahir et al., 2008). A number of dyes have been successfully adsorbed to water hyacinth *Eichhornia crassipes* (El Zavahry & Kamel, 2004). Leaf powder from the tree *Ricinus communis* L. has been used as a biosorbent for mercury removal (Al Rmalli et al., 2008).

Adsorption of a basic dye on crushed and screened wheat bran has been studied (Sulak et al., 2007). They found that wheat bran had an irregular and porous surface indicating high surface area and results suggested that dye was held by chemical activation or chemisorption to the wheat bran. Initial concentration of the dye solution had importance, as the amount adsorbed dye increased with increased initial concentration. Adsorbent dosage did also influence the adsorption, where amount of dye adsorbed per unit weight of adsorbent decreased with increasing adsorbent concentration from 2 g l^{-1} to 8 g l^{-1}. On the other hand, the percentage of colour removed increased with increasing adsorbent addition from 2 g l^{-1} to 8 g l^{-1}. Particle size of adsorbent did not have any significant effect on dye adsorption to wheat bran.

Pre-treatment or activation of plant materials can increase the specific surface and adsorption capacity of the materials. Adsorption of dyes containing a sulfonic group to Brazilian pine-fruit shell increased when the material was activated with acid or chromium (Lima et al., 2008). However, the environmental effects and cost of such pretreatment must also be considered when comparing the efficiency of different materials to remove polluting textile dyes from water.

1.3.2.2 Clays as adsorbents

The potential of clays to adsorb various pollutants has been studied and reported in several papers. Dali-Yousef et al. (2006) studied adsorption of organic compounds, for example a red dye, to local Algerian clays. The use of alkaline clays for heavy metal removal from water and waste water has been studied in Malawi (Sajidu, 2007). Potential use of some clay soils from Mali for heavy metal removal has been studied by Sällström (2008). Yeh et al. (1995) studied adsorption of disperse-red-60 dye to powdered diatomite, a biogenic sediment mainly consisting of porous siliceous algae skeletons.

As in the case of plant materials, adsorption capacity can be increased through activation of clay minerals. Dali-Youcef et al. (2006) showed increased adsorption of a red dye to dam sediments activated with ammonium chloride and bentonite activated with sulfuric acid. Armagan et al. (2003) found that three reactive dyes did not adsorb significantly to natural sepiolite, but high adsorption capacity was found when the sepiolite was modified with quartenary amines. Özdemir et al. (2004) studied the adsorption of three reactive azo dyes to sepiolite and zeolite. They concluded that the minerals in their natural form did not efficiently adsorb azo dyes due to electrostatic repulsion of the anionic dyes by the negatively charged minerals and in the case of zeolite, an exclusion of large molecules such as azo-dyes from the micropores in the mineral. However, when treated with quaternary amines, the adsorbability of reactive dyes was substantially improved, due to formation of a bilayer with positively charged quaternary amines electrostatically attracting the anionic dyes. Zahn et al. (2008) obtained increased adsorption of anionic dyes to diatomite when it was activated with magnesium hydroxide.

1.3.3 Water treatment to remove textile dyes

The efficiency of different water treatment methods to remove textile dyeing effluents depends on the chemical properties of the dyes. In general, textile dyeing generates effluents of great chemical complexity, a challenge in waste water treatment. The effluents contain a great variety of dyes, process aids and finishing products (Vandevivere et al., 1998). Many dyes used are stable to light, oxidation and anaerobic digestion (Gupta et al., 2003). Reactive dyes are highly soluble in water which makes them difficult to remove by conventional coagulation or through the activated sludge process (Özdemir et al., 2004; Chern & Huang, 1998).

Alternative treatment processes commonly used for waste water treatment in the textile industry are oxidation and adsorption (Özdemir et al., 2004). Granular activated carbon is the most widely used adsorbent (Dincer et al., 2007) with excellent adsorption properties. Venkata Mohan et al. (2002) studied different coal based sorbents and activated carbon, and found that activated carbon was most efficient in colour removal with a sorption capacity of 84 %. Lignite coal and bituminous coal had sorption capacities of about 23 %. However, extensive use of activated carbon is expensive (Lima et al., 2008), making the method unsuitable for large scale application and in small scale where economic resources are limited. In this context interest for cheap biosorbents has grown.

1.3.3.1 Treatment of textile dye effluents in Bamako

A system for treatment of water from artisanal textile dyeing units must be simple and cheap. A problem for development of a water treatment method is the lack of knowledge of the chemical composition of dye effluents.

A proposal for water treatment in Bamako has been made and studied with effluents from *Tantou Teinturie* (Diarra, 2006), which is a somewhat bigger dyeing unit than the units studied in this thesis. The proposed system includes a decantation pond, where the water stays 1½ to 2 hours, followed by two alternately used ponds where the water is mixed with carbonate, intensively stirred some minutes and then left for decantation. Finally the water is passed through a sand filter before it is emitted to the recipient. Results from experiments show that the system reduces COD about 70 %, suspended solids almost 100 % and turbidity and colour about 90%. However, the pH value was not reduced and the conductivity was somewhat increased due to the introduction of carbonate in the treatment process.

2 Materials and methods

This section presents the activities at the sites where textile dye effluents were sampled, the materials investigated as potential adsorbents or coagulants, and the methods used in the analyses.

2.1 Study sites

Effluents of textile dyes used for analysis were collected from three different sites in Bamako (Fig. 4). Two sites are located on the river side of the Niger River while the third is located in a housing area quite far from the river.

2.1.1 Torokorobougou

At the site in Torokorobougou (1) about a hundred women are working with dyeing. Dyeing is performed in metal basins heated with firewood. The site is located by the riverside and residual dye-baths are spilled directly to the river. Dyed tissues are washed in the river. Figs. 5 a), b) and d) show the dyeing activity in Torokorobougou. The dyestuffs used are bought from a dye vendor at the site.

2.1.2 Badalabougou

In Badalabougou (2) a smaller group of women, about 20, work with dyeing by the river side. Also here dyeing is performed in metal basins heated with firewood, residual dye-baths spilled directly to the river and dyed tissues washed in the river. Fig. 5 c) shows dye effluent sampling in Badalabougou.

Figure 4. Map of Bamako. *Commune V* is highlighted. Red circles represents sampling sites. 1) Torokorobougou, 2) Badalabougou and 3) Oulofobougou. Modified from République du Mali (2005).

a)

b)

c)

d)

Figure 5. The study sites. a), b) and d): Textile dyeing on the Niger River side in Torokorobougou (1); c): Sampling of dye effluents in Badalabougou (2).

2.1.3 Ouolofobougou Bolibana

The textile dyeing unit in Ouolofobougou Bolibana (3) is much smaller compared to the two other and consists of a family. Two women married to the same man started the dyeing activity in 1981. When the third wife came to the family and also started dyeing, the business grew. Until two years ago, effluents from the dyeing was emitted directly to the streets. Demands from the Ministery of Environment and Health resulted in the construction of a soakaway where all dye effluents are collected. The cement and brick construction is sealed with a plastic material to avoid leaching. This

Figure 6. Sampling of dye effluents in Oloufobougou (3).

dyeing unit and its activity has been described in a recent book (Gérimont, 2008). Contacts with Gérimont made the dyers change from buying dyestuff from an itinerant vendor to buying dyestuffs from the company Afrikolor. Fig. 6 shows sampling from the soakaway in Ouolofobougou.

2.2 Materials

The performance of several different materials in removal of textile dyes was tested. This section presents the materials used.

2.2.1 Laterite

Laterite is a common name for the thick layer of weathered material covering the fresh rocks in most tropical regions (Roquin et al., 1990). In Mali this weathered mantle can be as thick as 50-150 meters. The average mineral composition of laterites from southern Mali computed from major element chemical analyses is 43 % kaolinite, 24 % quartz, 21% hematite and 10 % goethite (Roquin et al., 1990). Laterite sampled from *Zone Kabala* was used in this study. Scanning electron microscopy (SEM) with X-ray fluorescence detector showed that laterite used mainly contained aluminium, silicon and iron, except for carbon, oxygen, hydrogen and nitrogen which can not be detected.. Traces of titanium were found and some particles contained high amount of zirconium.

Laterite pieces were pestled to a powder and then sieved to form two different fractions; particles < 800 µm and particles < 250 µm. Fig. 8 shows laterite before pestling and SEM images of laterite powder. For complete results from SEM see Appendix 11.

2.2.2 Rice bran and chaff

Rice bran and chaff were sampled from a rice mill in *Zone Industrielle* in Bamako. Rice bran was dried in 105 °C for about 24 hours to facilitate sieving. Rice chaff was applied to effluents without any pre-treatment, as well as in grinded form. Rice bran and grinded rice chaff were sieved through a 800 µm sieve before application. Rice chaff is shown in Fig. 7, powdered rice bran and SEM images of powdered rice bran in Fig. 9. For results from SEM analysis see Appendix 12.

2.2.3 Activated carbon

Activated carbon was tested both in the form of powdered activated carbon (PAC) and as granulated activated carbon (GAC).

2.2.4 Activated bentonite

Potential of bentonite for treatment of textile dye effluents was studied for activated bentonite from South Africa (240 FF).

2.2.5 Hydrolyzing metal salts

Performance of hydrolyzing metal salts commonly used in water treatment in treatment of textile dye effluents was also studied. Two different concentrations of aluminium sulfate and iron(III) chloride were applied.

2.3 Methods

Properties of river water, dye effluents and dyestuffs as well as performance of different materials in colour removal were analysed in several experiments both at *Université de Bamako* and at SLU, Uppsala. The methods used are described in this section.

2.3.1 Properties of river water

At the site in Torokorobougou, river water was sampled right where the effluents of dye solution takes place, the spillage site. River water was also sampled on the opposite side of the small island visible in Fig. 4 (accessible in the dry season), before and after the water from the dyeing site enters the main path of the river. Conductivity, pH, total dissolved solids, TDS, (Sension 156 Multiparameter Meters HACH) turbidity (Cyberscan IR Turbidimeter TB1000, Eutech) and dissolved oxygen, DO, (Oxi 330 Oximeter, WTW) were measured on these samples.

2.3.2 Properties of dye effluents

Raw dye effluents from Torokorobougou (DE_T), Badalabougou (DE_B) and Oloufobougou (DE_O) were analysed by measuring pH, conductivity and TDS. When effluents were too concentrated to measure conductivity and TDS, measurements were made on diluted samples. For DE_B and DE_O, UV/Vis spectra were measured on diluted samples using Lambda2 UV/VIS Spectophotometer (Perkin-Elmer).

Figure 7. Rice chaff used in jar test.

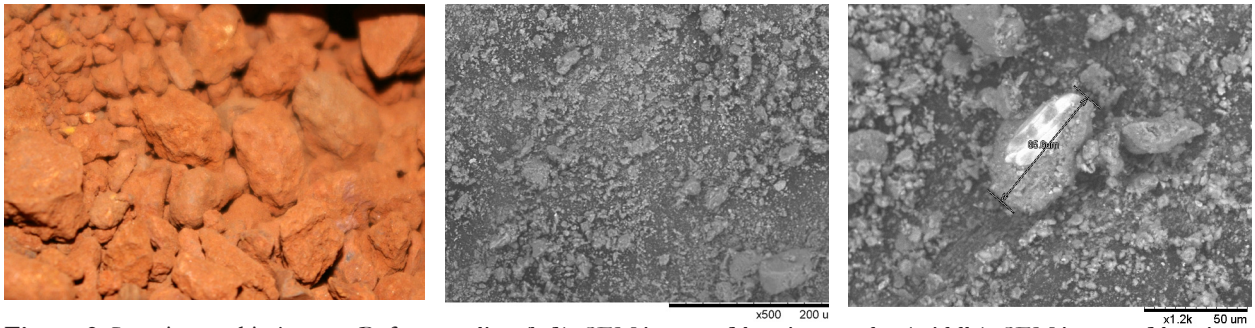


Figure 8. Laterite used in jar test. Before pestling (left), SEM image of laterite powder (middle), SEM image of laterite powder, (right). Marked particle has a diameter of 65 µm and contains approximately 27 % Zr (non-oxide mode).

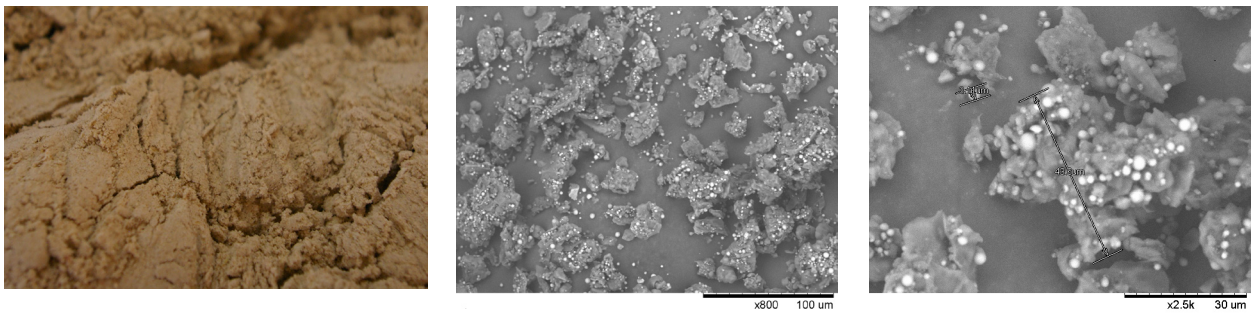


Figure 9. Rice bran used in jar test. Powder of rice bran (left), SEM images of rice bran powder (middle and right). Short arrow 3 µm, long arrow 44 µm.

2.3.3 Jar test

Efficiency of different materials as adsorbents or coagulation/flocculation agents was studied in jar tests. Table 4 presents the materials tested, their concentration and when applicable, the particle size. Data on what effluent was used for the test, its dilution and the initial pH is also shown. The initial concentrations of dye effluents from Badalabougou and Ouolofobougou were not the same. The effluent from Badalabougou was more concentrated; hence jar tests done with effluent from Ouolofobougou with dilution factor 50 represent a more diluted dye solution than jar tests made with effluent from Badalabougou with dilution factor 100. As the initial concentrations of dye stuffs are unknown, the relative difference in concentrations between the two effluents can not be given.

For comparison, diluted dye effluent without addition of any adsorbent or coagulant, and the different materials in distilled water (concentrations of materials 10 g l^{-1}) were also run in jar tests as blanks.

800 ml diluted dye effluent was put in beaker for jar test and 200 ml used for analysis of initial parameters. JLT6 Jar testing equipment (VELP Scientifica) was used to evaluate adsorption/coagulation-flocculation. After addition of material, the beakers were stirred with 250 revolutions per minute (rpm) for one hour to put the material in contact with the dye solution. Then the stirring

Table 4. Materials used in jar tests. Effluent B refers to effluent from Badalabougou and effluent O refers to effluent from Ouolofobougou.

Material	Concentration [g l^{-1}]	Start pH	Particle size [µm]	Effluent	Dilution factor
Activated bentonite	5	11.6		B	100
Activated bentonite	10	11.9		B	100
Activated bentonite	10	8.7		B	100
PAC	5	11.7		B	100
PAC	10	11.9		B	100
PAC	10	8.6		B	100
PAC	10	6.9		O	100
PAC	10	6.8		O	50
GAC	5	9.8		B	100
GAC	5	7.9		B	100
GAC	5	6.0		B	100
GAC	5	4.2		B	100
GAC	10	6.7		O	50
Rice bran	5	11.8	800	B	100
Rice bran	10	11.9	800	B	100
Rice bran	5	8.5	800	B	100
Rice chaff whole	5	6.7		O	50
Rice chaff whole	10	6.9		O	50
Rice chaff grained	5	6.8	800	O	50
Rice chaff grained	10	6.6	800	O	50
Laterite	5	6.7	250	O	50
Laterite	10	6.7	250	O	50
Laterite	5	6.7	800	O	50
Laterite	10	6.7	800	O	50
$Al_2(SO_4)_3$	0.3	11.8		B	100
$Al_2(SO_4)_3$	0.5	11.9		B	100
$Al_2(SO_4)_3$	0.5	8.4		B	100
$FeCl_3$	0.3	11.8		B	100
$FeCl_3$	0.5	12.0		B	100
$FeCl_3$	0.5	8.4		B	100

was decreased to 40 rpm for 15 minutes to make the flocs mature (in case of coagulation/flocculation). After 15 minutes stirring at 10 rpm the beakers were left for sedimentation. About 60 ml were sampled from each beaker for analysis of physico-chemical parameters after treatment. In some experiments, pH was adjusted to desired value using sulfuric acid.

Conductivity, TDS, pH (Sension 156 Multiparameter Meters HACH), DO (Oxi 330 Oximeter WTW) and turbidity (Cyberscan IR Turbidimeter TB1000, Eutech) was measured on the samples before and after jar test. Due to problems with equipment turbidity in later samples was measured with HI 93703 Microprocessor turbidity meter (HANNA instruments). However, samples before and after each jar test were analyzed with the same equipment. Turbidity was expressed in formazine turbidity unit (FTU). Temperatures in analysed samples ranged from 27 to 31 °C.

Further, absorption in the wavelength interval 800 to 200 nm and content of nickel, copper and zinc in samples before and after jar test with laterite, rice husk and activated carbon were analyzed. Absorption spectra were made with Lambda40 UV/VIS Spectrometer (Perkin Elmer) and metals were studied using Atomic Absorption Spectrometer AAnalyst200 (Perkin Elmer).

2.3.4 Chemical Oxygen Demand (COD)

COD was analyzed before and after jar tests with laterite, PAC, GAC and rice husk. The potassium dichromate method was used. 2 ml sample was put in a test tube and distilled water was used as the blank. About 0.1 g mercury sulfate was put in each tube as a catalyzer and 2 ml of concentrated $H_2SO_4 – Ag_2SO_4$ solution (50 g l^{-1}) was added. After adding 1 ml 0.04 M dichromate the tubes were closed, gently mixed and heated to 150 °C during 2 hours. The samples were left for cooling, then transferred to a measuring flask and diluted to 30 ml with distilled water. The diluted samples were put in beakers and 5 ml $H_2SO_4 – Ag_2SO_4$ solution was added. The samples were stirred and then left to cool before 2 drops of ferroine was added. The samples were titrated with 0.0125 mol l^{-1} iron(II) sulfate until the colour changed from blue-green to orange.

To verify the iron(II) sulfate, the dichromate was diluted ten times (to 0.004 mol l^{-1}). 10 ml of this solution was mixed with 20 ml distilled water. 5 ml $H_2SO_4 – Ag_2SO_4$ solution was added. The samples was stirred and then left to cool before 2 drops of ferroine was added. The solution was then titrated with 0.0125 mol l^{-1} iron(II) sulfate until the colour changed from blue-green to orange. COD for samples were calculated using Eq. 2, where X_{COD} is COD expressed in mg l^{-1}, V_1 is the volume iron sulfate used in the titration of the sample, V_B the volume iron sulfate used in the titration of the blanc and V_T the volume iron sulfate used in the titration of 0.004 M dichromate.

$$X_{COD} = \frac{[(V_T - V_1) - (V_T - V_B)]\ 1000}{V_T} = \frac{1000\ (V_B - V_1)}{V_T} \qquad \text{Eq. 2}$$

2.3.5 Properties of dyestuff

Analyses of chemical properties of dyestuffs were made with UV-Vis spectrophotometry (Lambda2 UV/VIS Spectophotometer, Perkin-Elmer), Nuclear Magnetic Resonance (NMR) spectroscopy (Bruker 400 MHz) and Scanning Electron Microscopy (SEM). Dyestuff solubility in alkaline and acidic environment was tested using 0.01 M sodium hydroxide and 0.01 M nitric acid, respectively.

2.3.5.1 Scanning Electron Microscopy

SEM is used to produce images of materials with a higher magnification than is possible with light microscopes. Light microscopes are limited by the fact that it is impossible to form an image of an object smaller than half the wavelength of the radiation used (Chang, 2005). Using electrons has the advantage over e.g. X-rays that electrons are charged and can be focused to produce an image.

The principles of SEM is that a beam of electrons is produced by an electron gun in the top of the instrument. The elecron path is directed in vacuum through electromagnetic fields and lenses focusing the beam toward the sample. When the beam hits the sample, electrons and X-rays are ejected and can be detected and transformed to an image on a screen.

Elementary analysis with the SEM instrument can detect elements with atomic number, $z \geq 11$ (See periodic table in Appendix 1). SEM measurements were performed using Hitachi TM-1000 microscope and data from elementary analysis interpreted with SwiftED-TM software.

2.3.6 Health aspects

Some data was collected through semi-structured interviews with people performing dyeing. This was not a major part of the work and the material collected not big enough to draw general conclusions, but it gave some additional insight to the importance of the textile dyeing activity and the perceived health effects.

3 Results

This section presents results from measurements of chemical characteristics of river water and untreated dye effluents from the three study sites. A large part of the section is devoted to results from jar tests with different materials. In the end some properties of dyestuffs used and perceived health effects of textile dyeing are presented.

3.1 Properties of river water

Table 5 shows properties of river water sampled in the vicinity of the dyeing activities in Torokorobougou. The results indicate that dye effluents increase pH, conductivity, TDS and turbidity, but decreases DO in river water. The water before entering the main path of the river and the river water at the entrance of the main path show similar properties. The water sampled at the spillage site had higher pH, conductivity, TDS and turbidity and lower DO than the river water.

Table 5. Physico-chemical properties of river water exposed to dye effluents. Numbers for spillage represents mean values for three samples from the area where dye solution is emptied in the river. TDS - Total Dissolved Solids; DO - Dissolved Oxygen.

	pH	Conductivity [µS cm^{-1}]	TDS [mg l^{-1}]	Turbidity [FTU]	DO [mg l^{-1}]
Spillage	8.0	160	72	11	2.4
River before entrance	7.3	44	19	4.4	5.8
River entrance	7.2	41	18	4.1	6.0

3.2 Properties of dye effluents

pH-values, conductivity and TDS for the raw dye effluents sampled are presented in Table 6. The UV-Vis absorption of the effluents sampled in Badalabougou and Ouolofobougou are presented in Figs. 11-12 and Figs. 13-14, respectively.

Table 6. Properties of untreated dye effluents. TDS - Total Dissolved Solids; DO - Dissolved Oxygen; DE_T - dye effluents from Torokorobougou, DE_B - dye effluents from Badalabougou; DE_O - dye effluents from Ouolofobougou.

	pH	Conductivity [mS cm^{-1}]	TDS [g l^{-1}]
DE_T	13,18	183	81
DE_B	13,68	149	150
DE_O	12,54	10,5	5.4

3.3 Jar tests

The dye effluents diluted 100 times had initial pH-values within the range 11.6 to 12.0. In the jar tests with bentonite (5 and 10 g l^{-1}), PAC (5 and 10 g l^{-1}), rice bran (5 and 10 g l^{-1}), aluminum sulfate (0.3 and 0.5 g l^{-1}) and iron(III) chloride (0.3 g l^{-1} and 0.5 g l^{-1}), visible reduction of colour was only obtained with iron(III) chloride treatment.

Iron(III) chloride reduced the pH with about 10 pH units for both concentrations, the reduction was somewhat higher for the higher concentration. Bentonite reduced the pH with 1.4 and 1.8 pH-units in the two tests, respectively. The other materials showed only slight differences in pH.

Bentonite reduced the conductivity about 1.1 mS cm^{-1} in both concentrations, while iron(III) chloride increased the conductivity 4.3 and 7.3 mS cm^{-1} respectively for the two concentrations. PAC,

rice bran and aluminium sulphate only sligtly decreased the conductivity.

Iron(III) chloride decreased the turbidity almost 30 FTU. PAC decreased the turbidity 7.5 FTU when added in the lower concentration, but increased the turbidity 7.5 FTU when added in higher concentration. Rice bran increased the turbidity importantly, about 290 FTU in both tests while bentonite increased turbidity 57 FTU when added in the lower concentration, and 92 FTU when added in the higher concentration. Aluminium sulphate did only slightly change the turbidity. Raw data from these jar tests is presented in Appendix 2. Figure 10 shows beakers after jar test with bentonite, PAC, rice bran, aluminium sulfate and iron(III) chloride.

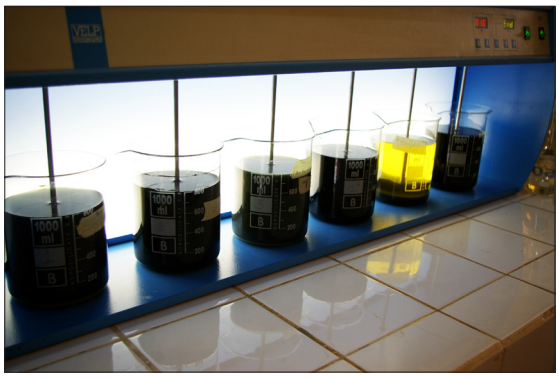


Figure 10. Jar test with DE_B. From left to right: Bentonite, PAC, rice bran, aluminium sulfate, iron(III) chloride and blank. As can be clearly seen, iron(III) chloride efficiently coagulated dye effluents.

3.3.1 Adjusted pH in dye effluents

When the initial pH-values of the dye effluents were adjusted to 8.55 ± 0.15, addition of iron(III) chloride still caused the most evident visible colour removal, but also activated carbon made the water somewhat clearer. Iron(III) chloride caused the largest decrease in pH, ending on pH 1.8, regardless if the pH was adjusted or not. Aluminium sulphate reduced the pH 2 units when initial pH was adjusted. Bentonite caused a similar pH decrease with and without adjusted initial pH while PAC slightly increased the pH when initial pH was adjusted.

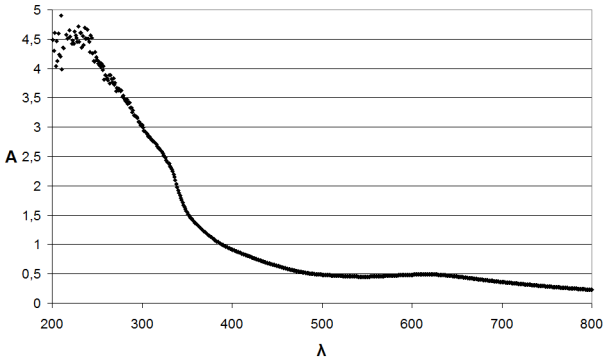


Figure 11. UV-Vis absorption spectra for mixed dye effluents sampled in Badalabougou.

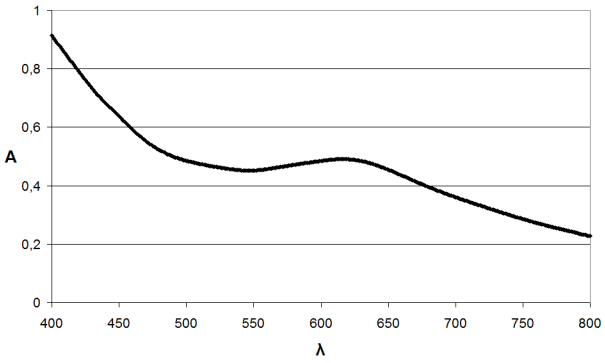


Figure 12. Visible absorption spectra for mixed dye effluent sampled in Badalabougou.

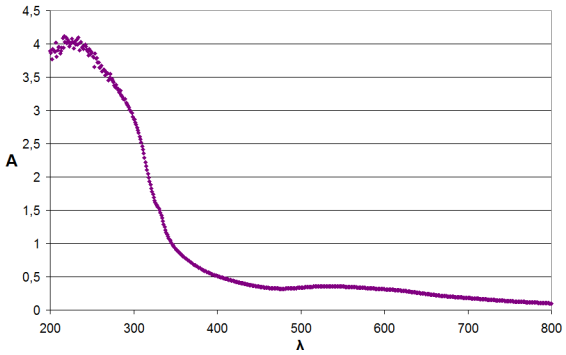


Figure 13. UV-Vis absorption spectra for mixed dye effluents sampled in Ouolofobougou.

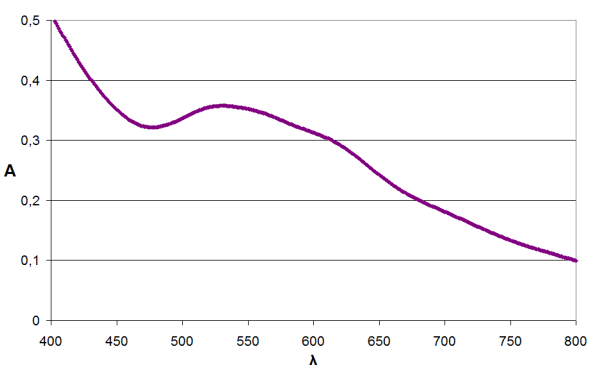


Figure 14. Visible absorption spectra for mixed dye effluent sampled in Ouolofobougou.

Conductivity increased 9 mS cm^{-1} for the iron(III) chloride treated sample when initial pH was adjusted. Addition of bentonite slightly increased conductivity while PAC, rice bran and aluminium sulphate did not change the conductivity.

Iron(III) chloride and PAC decreased turbidity, about 30 and 15 FTU respectively. Rice bran, bentonite and aluminium sulphate increased turbidity, about 200, 80 and 30 FTU respectively.

Bentonite decreased TDS when added to samples with unaltered pH, 540 mg l^{-1} decrease when 5 mg l^{-1} was added and 570 mg l^{-1} when 10 g l^{-1} was added. When pH was adjusted to 8.7 before jar test, addition of bentonite increased TDS 150 mg l^{-1}. Raw data from this jar test is presented in Appendix 3.

3.3.2 pH effect on adsorption to GAC

Jar tests with addition of GAC to diluted dye effluent adjusted to different pH values (pH 10, 8, 6 and 4) did not prove an influence of pH on changes in parameters analysed. However, absorption spectra were not established for these samples, hence information on colour removal is lacking. pH-values were almost unchanged before and after jar test, except for the sample with pH 4, where pH had increased 2 units after jar test. TDS increased for all pH values, about 70 mg l^{-1} for pH 10 and 8, and about 90 mg l^{-1} for pH 6 and 4. Turbidity was almost unchanged in the jar test. Raw data from this jar test is presented in Appendix 4.

3.3.3 Rice chaff, PAC, GAC and Laterite in samples with adjusted pH

Untreated diluted dye effluents did not show any absorption peak in the visible spectra (400-700 nm), which was unexpected as the solution was slightly purple-black. However, all samples before jar test absorbed in the UV-range, with a peak at 227 nm (Figs. 15-18). Addition of rice chaff to the effluents did not decrease the UV-absorption in the samples, neither when added in untreated form nor when grinded. Fig. 15 shows absorption spectra for DE_O treated with rice chaff. Rice chaff in

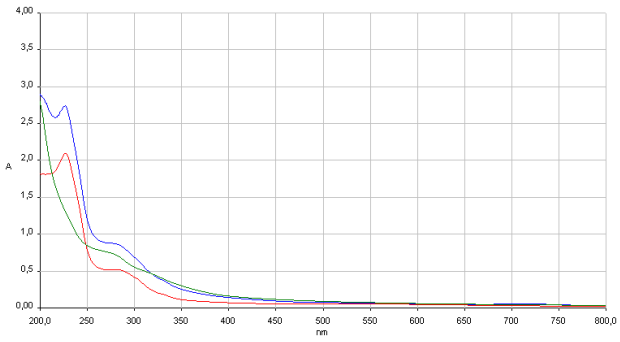


Figure 15. Absorption spectra for DE_O treated with rice chaff. Red line: effluent before jar test, blue line: after jar test, green line: rice husk in distilled water.

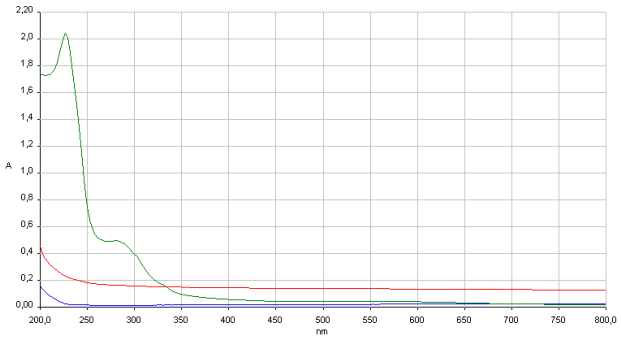


Figure 16. Absorption spectra for DE_O treated with PAC. Green line: effluent before jar test, red line: after jar test, blue line: PAC in distilled water.

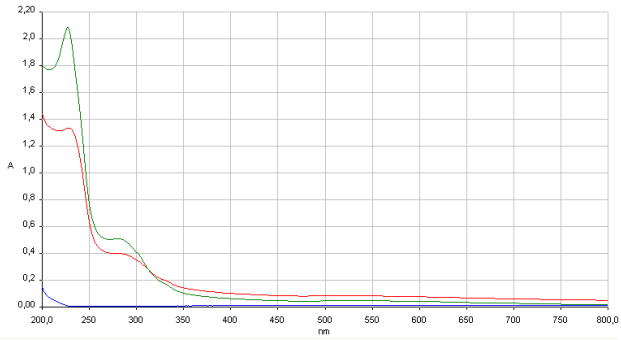


Figure 17. Absorption spectra for DE_O treated with GAC. Green line: effluent before jar test, red line: after jar test, blue line: GAC in distilled water.

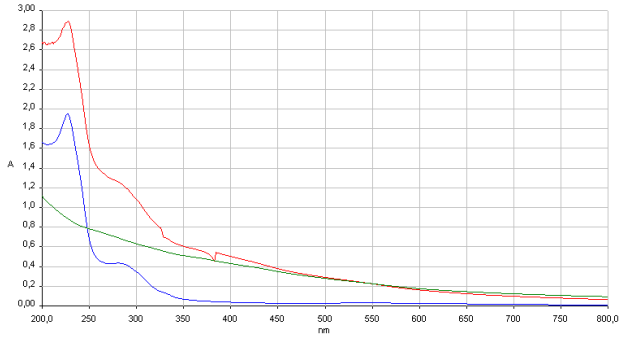


Figure 18. Absorption spectra for DE_O treated with laterite powder < 800 µm. Blue line: effluent before jar test, red line: after jar test, green line: laterite in distilled water.

distilled water showed increasing absorption from 350 nm to 200 nm, sharply increasing from 250 nm to 200 nm. This curve can explain the increased absorption in effluent sample after jar test compared to before jar test. The pattern is the same for untreated rice chaff and grinded rice chaff, but absorption is higher for grinded rice chaff. The pH was almost constant before and after jar test for both concentrations of rice chaff, but addition increased conductivity (57 and 93 µS cm^{-1} increase for 5 and 10 g l^{-1} respectively), TDS (24 and 41 mg l^{-1} increase respectively) and turbidity (6 and 11 FTU increase respectively). COD increased after addition of rice chaff, about 120 mg l^{-1} for addition of 5 g l^{-1} and 125 mg l^{-1} for addition of 10 g l^{-1}.

Activated carbon decreased the absorption when added to diluted dye effluents both in form of powder (Fig. 16) and in granulated form (Fig. 17). PAC is most efficient in reducing the absorption peak. Addition of PAC and GAC increased pH with almost 3 units. Conductivity and TDS increased as well, about 115 µS cm^{-1} and 50 mg l^{-1} respectively for PAC and about 215 µS cm^{-1} and 95 mg l^{-1} for GAC. Addition of PAC increased turbidity about 40 FTU in sample diluted 100 times and 60 FTU in sample diluted 50 times. Addition of GAC increased turbidity about 20 FTU. COD in samples was lower after jar test with activated carbon. PAC decreased COD about 40 mg l^{-1} and GAC decreased COD about 5 mg l^{-1}.

Addition of laterite to the effluents did not decrease the UV-Vis absorption in the samples. The absorption at absorption maximum (227 nm) increased after jar test with the same intensity as the absorption of laterite in distilled water at the same wavelength (Fig. 18), indicating that no reduction of colorant has taken place. No important changes of pH, conductivity and TDS were observed when comparing samples before and after jar test. Turbidity increased after addition of laterite, about 200 FTU when 5 g l^{-1} was added and almost 500 FTU when 10 g l^{-1} was added. Addition of laterite in distilled water (10 g l^{-1}) increased turbidity 340 FTU.

Analyses of the metal content in effluent samples before and after treatment with activated

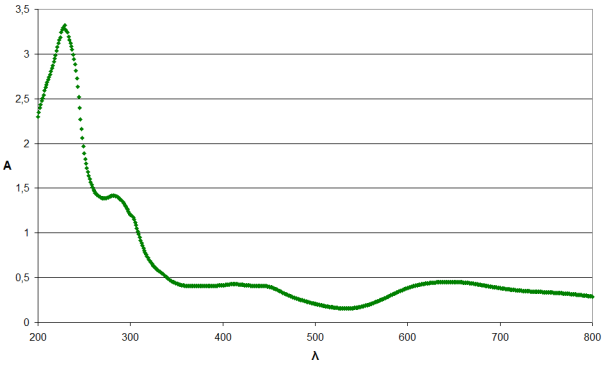


Figure 19. UV-Vis absorption spectrum for green dyestuff.

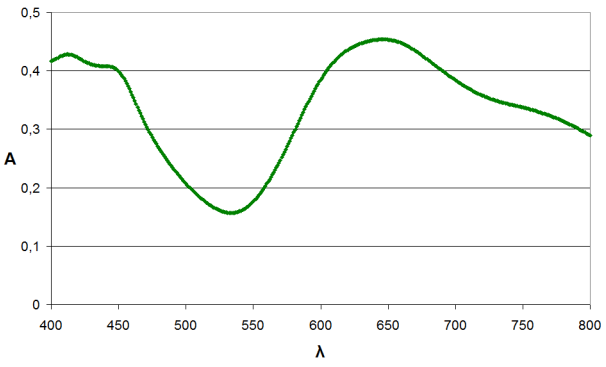


Figure 20. Visible absorption spectrum for green dyestuff

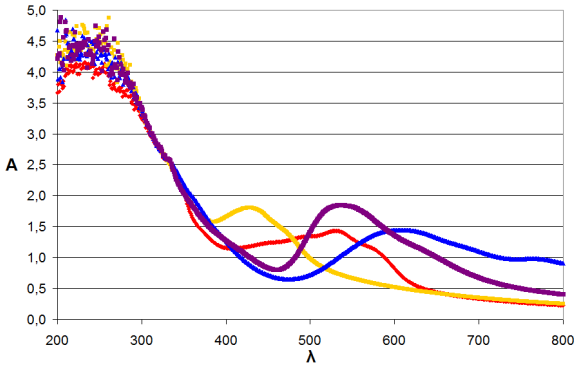


Figure 21. UV-Vis absorption spectra for red, yellow, blue and purple dyestuffs.

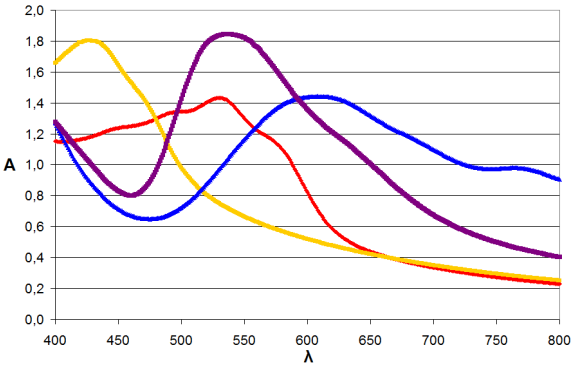
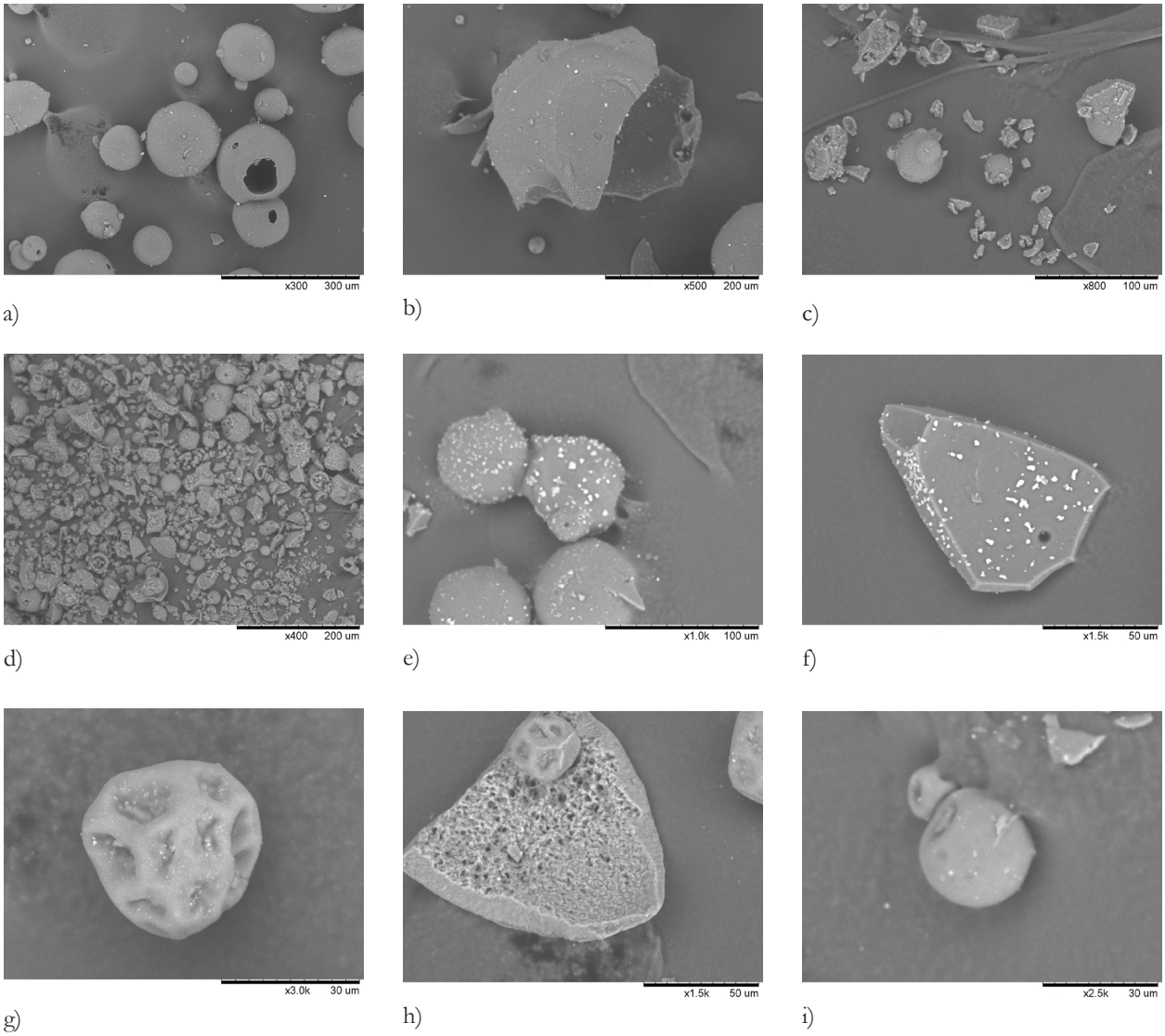


Figure 22. Visible absorption spectra for red, yellow, blue and purple dyestuffs.



a) b) c)

d) e) f)

g) h) i)

Figure 23. Selected SEM images of dyestuffs. a) and b) green dyestuff; c) and d) yellow dyestuff; e) and f) blue dyestuff; g) and h) purple dyestuff; i) red dyestuff.

carbon, rice chaff and laterite detected no presence of copper. Nickel was detected in concentrations about 2.3 to 2.6 mg l^{-1} in all samples from the jar tests, there were no difference before and after jar test for any material. The same pattern was observed for zinc but in this case the concentration in samples ranged from 0.20 to 0.26 mg l^{-1}. Nickel and zinc concentrations detected in water samples from the spilling site in Torokorobougou were lower than concentrations in diluted dye effluents (0.63 to 1.1 mg l^{-1} for nickel and 0.06 to 0.17 mg l^{-1} for zinc). Raw data from jar tests is presented in Appendix 5.

3.4 Dyestuff properties

UV-Vis spectum for green dyestuff is shown in Figs. 19-20. The dyestuff is soluble in both water and 0.01 M sodium hydroxide, and has the same UV-Vis spectrum for the two pH values (7.6 and 12). The dyestuff is also soluble in 0.01 M nitric acid (pH 1.8) and no visible colour difference was observed.

UV-Vis spectra for red, yellow, blue and purple dyestuffs dissolved in distilled water are presented in Figs. 21-22. All dyestuffs were also soluble in 0.01 M sodium hydroxide and 0.01 M nitric acid, with no colour change.

Analyses with X-ray fluorescence detector connected to SEM showed that dyestuffs mainly consist of the elements sulfur, chlorine and sodium, except for carbon, oxygen, nitrogen and

hydrogen which can not be detected. Green dyestuff did also contain relatively high amounts of barium. Minor fractions of aluminium and silicon were found in several dyestuffs. Small amounts of chromium were found in red and yellow dyestuffs, and in the latter traces of vanadium and iron were detected. SEM images of particles in green, yellow, blue, purple and red dyestuffs are shown in Fig. 23. Complete results from SEM analyses of dyestuffs are presented in Appendices 6-10. For positions of elements in the periodic table see Appendix 1.

NMR analysis of dissolved green dyestuff showed signals for aromatic structures and methyl groups. The relaxation was fast, which could indicate large molecules, but could also be an effect of impurities in the sample.

3.5 Health aspects

Health aspects for the women working with textile dyeing were not the focus for this thesis. However, the following section presents some observations of what women working with dyeing at the three study sites say about their health in relation to their work, and what type of protection they use.

One woman dyeing in Oloufobougou, who has participated in workshops on health effects of exposure to different chemical substances, relates several health problems to exposure to dyestuffs. Women working with dyeing in Torokorobougou relate some skin problems on hands to the sodium hydroxide used in the dyeing process. They talk about skin problems on hands and feet as something mostly occuring when you start working with dyeing, since after a while, the skin adapts to the abnormal working conditions.

One woman in Torokorobougou says she has not seen effects of inhalation from dye baths. Respiratory problems are otherwise discussed as a long term effect of exposure to dye vapour, and at the site in Badalabougou some women use masks for protection. However, these masks are not suited for this kind of use. The woman in Ouolofobougou says she knows people working with masks, but she feels she can not work properly wearing a mask. Gloves are used by the women at all three sites, but not by everybody. Even women wearing gloves have often direct contact with dye solution as it enters the gloves, which are emptied now and then.

Sodium hydroxide in high concentrations has both acute and long term health effecs. Inhalation of volitile sodium hydroxide cause smarting pain, cough, respiratory problems and might damage the lungs (*Skyddshandb.*, 1979). Long-term exposure might cause chronical bronchitis. Sodium hydroxide is very caustic for skin and eyes, and ingestion causes internal injuries. Long term exposure to less concentrated solutions might cause eczema and skin problems.

4 Discussion

Knowledge of cheap treatment methods for artisanal waste water is scarce. Most of the literature deals with either treatment methods for textile dyeing effluents in an industrial scale, or small scale drinking water purification. Methods for treatment of effluents from small-scale activities such as textile dyeing are not often discussed.

This Master's Thesis project did not find a suitable material for the treatment of small-scale textile dyeing effluents. However, hopefully it has increased the knowledge in the field and identified routes for future research. One major obstacle for finding a material efficient in dye removal is the lack of knowledge of the chemical identity of the dyestuffs used.

4.1 Influence of physical and chemical parameters

Yeh & Thomas (1995) concluded that PAC was most efficient as adsorbent in colour and COD removal from textile dye effluents, GAC intermediate and diatomite least efficient. In my study, consistency in the methods used for evaluation of performance in dye effluent treatment is lacking; hence it is difficult to fully compare the different materials used. However, looking globally at all analyses made, the coagulant iron(III) chloride performed best as it made the water clear. PAC and GAC followed, as they removed compounds absorbing UV-radiation. No indication of dye removal with activated bentonite, laterite, rice bran, rice husk and aluminium sulfate was found.

These results might be due to the fact that materials used have no effect on dye effluents with the present, unknown composition. However, it is also possible that better results can be obtained with changed experimental conditions. In this section, effects of different parameters potentially influencing coagulation/flocculation and adsorption are discussed, in relation to results from previous research. Influence of concentration of material added is not discussed in detail, as a wide range of concentrations are used in different studies, nor is effect of dye concentration discussed, as jar tests were made on mixed dye effluents with unknown dye composition and dye concentration.

4.1.1 Effect of pH

No effect of pH on performance of coagulants/flocculants was observed in this study. The most efficient material to remove visible colour and turbidity in jar tests was iron(III) chloride, and the removal of turbidity was about the same for pH 11.9 and 8.4. Aboulhassan et al. (2005) found that optimal conditions for coagulation of textile effluents from a factory in Morocco were pH 8 for iron(III) chloride and pH 7 for aluminium sulfate, added in doses of 200 mg l^{-1} for both coagulants. The two concentrations tested in my study, 0.3 g l^{-1} and 0.5 g l^{-1} gave approximately the same visible colour and turbidity removal. Aboulhassan et al. (2005) found aluminium sulfate to be very efficient in removal of COD but less effective in removal of colour. COD before and after jar test was not analyzed for these samples.

It would be interesting to test performance of the coagulants even in acidic pH, as Harrelkas et al. (2009) found that optimal treatment conditions for turbidity removal from a dyeing plant effluent with aluminium sulfate were pH 5 and an aluminium sulfate concentration of 100 mg l^{-1}. In jar tests presented in this thesis, aluminium sulfate did neither remove colour nor turbidity.

The pH effect on adsorption to GAC was tested but did not show any clear differences in the pH range 4-10. Similar results were obtained by McKay (1982) where adsorption of telon blue to GAC was only slightly or not at all influenced by pH ranging from 5.2 to 8.5. Adsorption of a basic dye to wheat bran was not significantly influenced by pH in a study by Sulak et al. (2007). Attia et al. (2004) observed increasing adsorption of metylene blue and congo red to activated carbon when pH was increased from 3 to 6, but with further increase in pH adsorption decreased. Effect of pH on adsorption depends on adsorbates and adsorbents involved in the system.

4.1.2 Contact time

For adsorption of pollutants to different materials, contact time between adsorbate and adsorbent might be an important factor, depending on time needed to reach equilibrium in the system. The contact time between effluent and adsorbent used in this study (1.5 h during stirring) could be too short for efficient dye removal. McKay (1982) used an equilibrium time of five days in a study of dyestuff removal from aqueous solution with granular activated carbon. However, Yeh & Thomas (1995) concluded that colour removal reached equilibrium within 2 h contact time for both GAC and PAC. Adsorption of a basic dye to wheat bran increased with contact time but reached equilibrium after about 20 minutes (Sulak et al., 2007). Attia et al. (2004) concluded from kinetic measurements that 90-96 % of the adsorption of methylene blue and congo red to activated carbon took place within 1 h.

4.1.3 Temperature

Temperature of dye effluents when treated is also an aspect to consider, but was not done in this study. All jar tests were performed under ambient temperature, about 30 °C. McKay (1982) observed an increasing rate of dye uptake with increasing effluent temperatures (in the range 20-80 °C) due to an increase in diffusion coefficient with increasing temperature; hence increased adsorption rate. Increase of temperature from 30 to 50 °C increased adsorption of a basic dye to wheat bran in a study by Sulak et al. (2007). On the contrary, Attia et al. (2004) observed decreased adsorption of metylene blue and congo red to activated carbon when the temperature was increased from 30 to 40 and 50 °C, respectively.

4.2 Dyestuff identity

Investigations of the properties of dyestuff bought in Bamako did not reveal their identity. NMR analyses of the green dyestuff indicate that the colorant is an organic molecule with aromatic structures. Elementary analysis with SEM showed that the green dyestuff contained relatively high amount of barium. Barium chloride is used in pigment and textile dye manufacturing (USHHS, 2007). Typical concentration of active ingredient in dyestuffs ranges from 20 to 80 % (USEPA, 1996).

The potential negative health effects of barium in water depend on in what form barium is present. Compounds such as barium sulfate that are not easily dissolved, are normally not harmful (USHHS, 2007). Soluble compounds such as barium chloride can enter the body and can in very high concentrations cause changes in the hearth rhythm and paralysis. Long term effects of ingestion of lower barium concentrations is not well studied on humans, but experiments with rats showed decreased kidney function, decreased body weight and decreased survival.

Description of the dyeing process in Ouolofobougou (Gérimont, 2008) indicates that the dyes used in this unit probably are vat dyes, but this is not the case for the dyestuffs analysed, as they are water soluble. Treatment methods described in reference articles discuss mainly other classes of dyestuffs than vat dyes.

4.3 Results in relationship to guideline values

Zinc concentrations in surface water and ground water normally does not exceed 0.01 mg l^{-1} and 0.04 mg l^{-1}, respectively (WHO, 2003). This means that zinc concentrations both in effluents from Ouolofobougou (0.20-0.26 mg l^{-1}) and in samples from river water at the spilling site in Torokorobougou (0.06-0.17 mg l^{-1}) exceed these normal concentrations.

Nickel concentration in surface water and ground water varies and depends for example on land use and pH. The WHO guideline value for nickel in drinking water is 0.07 mg l^{-1} and a calculated value for general toxicity is 0.13 mg l^{-1} (WHO, 2005). These concentrations are greatly exceeded in both effluent samples (2.3-2.6 mg l^{-1}) and water at the spilling site (0.63-1.1 mg l^{-1}).

Analysis of green dyestuff indicated a relatively high content of barium. The concentration of

barium ions in effluents is not known, but the WHO guideline value for drinking water is 0.7 mg l^{-1} (WHO, 2004).

4.4 Methods

Adsorption spectra were useful to evaluate the capacity of different materials to adsorb UV-absorbing compounds from samples. However, such spectra were not established for tests of all materials, hence information on possible removal with bentonite, rice bran, aluminium sulphate and iron chloride is missing, as well as potential influence of pH on removal with GAC. It would have been valuable to have these data to compare performance of different materials that might remove dyes but not show desired results in change of pH, conductivity, TDS and turbidity.

It would have been interesting to have spectral data from treatment with bentonite to compare with spectra for PAC before and after jar test. Spectra for PAC before and after jar test indicate removal of compounds absorbing in the UV-range during treatment even though change in pH, conductivity, TDS and turbidity did not show promising results for this material. These parameters were not promising for bentonite either, except for decrease in TDS, but for bentonite no absorption spectrum was made; hence no conclusions can be drawn concerning removal of UV-absorbing compounds. However, Pala & Tokat (2002) found that addition of PAC to an activated sludge system improved the colour removal, while addition of bentonite did not significantly improve colour removal.

Samples of dye effluents and river water from the different sites were stored in the laboratory under ambient temperature (about 30 °C). All jar tests were not performed on the same effluents and not at the same time, making the different compositions of dye effluents and potential chemical changes over time sources of uncertainty.

Determination of COD with the potassium dichromate method includes uncertainties as small errors in the titration might change the results and a measuring flask was used for dilution. A report from the European Commission (2003) points out the high organic load in textile dye effluents and that it is usually expressed as COD and BOD, but that it could be better expressed as TOC and DOC. If equipment to analyse TOC and DOC is available, this might be a better alternative, also reducing the handling of mercury.

The focus for this thesis work was to find a cheap, accessible material that could be used for treatment of the mixed effluents sampled from residual solutions of artisanal textile dyeing. This is good from a perspective of applicability. However, the fact that no good solution was found indicates the necessity of reducing the parameters in the system. Chemistry of dyestuffs needs to be understood, and potential treatment methods for the different compounds found in mixed effluent developed. Firstly, it is important to know what chemical compounds give the colour in the dyestuff and what other compounds are added. Secondly, adsorption and coagulation/flocculation studies can be made for each dye dissolved in distilled water, to analyze the potential for different materials in treatment of a simple effluent.

With this information and knowledge of the importance of parameters such as those discussed in Chapter 4.1, further studies to find a method working in practice could be designed. Papić et al. (2004) studied colour removal from a synthetic waste water prepared by dissolving two known reactive dyes in distilled water. They observed colour removal higher than 90 % for aluminium chloride doses > 0.4 g l^{-1} and pH ranging from 3.5 to 5.0. Almost complete colour removal was obtained with a combination of aluminium coagulation and adsorption to PAC. These results could not be implemented in practice directly, as they are made on prepared wastewater containing known dyes, but gives information of performance of a coagulant. The results also enlighten possible benefits in combining different materials and mechanisms to optimize treatment of effluents.

Iron(III) chloride showed highest potential to decrease visible colour, but gave a yellow-brownish colour to the water and a low pH, properties that might not be desired for effluent treated at the sites. If dye removal is improved with an altered pH, the additive used to change pH in the effluents must also be cheap and available for the method to be implemented.

4.5 Results in a socio-economic context

Improving the environmental and health aspects of textile dyeing in Bamako is as much a question of socio-economic conditions and communication as of science. Finding a treatment method that works chemically would be an important step, but the material must be cheap and available and the method accepted to be implemented. One woman at one of the sites said that people from the university only come and take pictures, after that nothing happens. At another time of sampling a dye vendor thought we were from a ministry and was consequently not positive to the sampling. These episodes indicate the importance of communication between university staff and people working with dyeing. The objective of the research and how the research process and results could affect dyers should be clearly stated, as well as the fact that the road from identification of a problem to a working solution often is very long. Communication is mentioned in the PRSP as important for a better, decentralized and participatory management of natural resources and environmental protection (République du Mali, 2006). People working with dyeing are also an important resource for information on practices applied and health aspects.

The policy and legislation concerning water quality and effluents of toxic substances seems to be good in theory, the main problem is that it is not implemented. Strengthening of the human resources in responsible ministries and directions as well as decreased corruption is important for an efficient implementation. The fact that quantity and quality of personnel is lacking in responsible governmental bodies at the same time as students with diploma in natural sciences face difficulties in finding employment shows that efficiency in regulations is a complex issue.

Efficient implementation of policy and legislation is not the only aspect for a sustainable solution of the situation. If laws are followed, a lot of women without access to the formal sector will loose the possibility to earn their livelihood. Further, the cultural importance of *bazins* makes a ban of the dyeing activity impossible. Gérimont (2008) classes this as a popular cultural expression used by people from all social classes; dyeing made in Africa for Africans, not for tourists.

A risk is that interventions to decrease negative impact of dyeing effluents only result in a replacement of the problem. The soakaway installed at the dyeing unit in Ouolofobougou is excavated when filled and the effluents transported and dumped outside the city. However, some kind of construction to collect the effluents is necessary to be able to introduce a treatment method with any material with potential for colour removal. Such installations might be impossible for economic reasons for a lot of people working with dyeing. Installation of the soakaway in Ouolofobougou cost 1 300,000 Franc CFA (1,985 €), which the dyers managed to pay through micro finances.

4.6 Future perspectives

A key issue for further research is to identify the chemical composition of the dyestuffs and additives used in the dyeing process, in order to find out what chemical processes could be used for treatment of the effluents. As the textile effluents are complex, one single material might not be sufficient. Hence work with combinations of different materials would be interesting. Harrelkas et al. (2009) investigated coupling of coagulation/flocculation with aluminium sulfate and membrane filtering or adsorption to powdered activated carbon as methods for treatment of textile dye effluents. They concluded that the best COD removal (> 80 %) was obtained through treatment with aluminium sulfate followed by adsorption to PAC, while the best colour removal (74 %) was obtained with aluminium sulfate coagulation followed by ultrafiltration. However, these materials are neither cheap nor widely accessible, making it necessary to find other solutions for the treatment of effluents from artisanal textile dying in Bamako.

A plant material used in other water treatment studies but not tested here is seeds from *Moringa oleifera*. There are no pure cultures of *M. oleifera* in Mali but it is cultivable and planted to some extent in the country (Fofana, 2009). As it is a multi-purpose tree with leaves rich in vitamins and suitable for the prevention of desertification, studies of the potential of *M. oliefera* to adsorb textile dyes could be interesting.

Attia et al. (2004) studied the potential of cotton stalks and activated carbon prepared from cotton stalks to adsorb dyes. As Mali is an important cotton producer, this agricultural rest material should be available. The study showed that untreated pieces of cotton stalks were not efficient to use as adsorbents, but after carbonization and activation with either zinc chloride or steam, adsorption capacity was high. Carbonization and activation of cheap, available materials might be a way to find adsorbents to treat dye effluents, if further studies on untreated materials do not give satisfying results. However, it must be emphasized that a working treatment method is to a large part dependent on a working infra-structure, not only on a chemical treatment method.

Health aspects of textile dyeing might soon be better known, as this issue will be studied during 2009 (Plea, 2009).

5 Conclusions

So far, no method has been found yielding satisfying results in treatment of effluents from small scale textile dyeing. Results from chemical analyses in this work show that iron(III) chloride can coagulate dye effluents making the water clear. Activated carbon showed some adsorption capacity of dye effluents, especially in the powdered form. Neither the locally available rice bran, rice chaff, and laterite, nor commonly used bentonite and aluminium sulfate removed colour from effluents in jar tests.

The chemical composition of the dyestuffs tested is still unknown, and ought to be investigated further when searching for a treatment method. Dyestuffs analysed in this study contained a lot of sulfur, chloride, sodium and, in the case of the green one, barium. NMR analyses of green dye solution indicated presence of aromatic molecules.

A significant fraction of the dyestuffs consists of substances which are not part of the colour-yielding dye. Effluents from the dyeing process are even more intricate as they contain added auxiliaries.

Mixed dye effluents had zinc and nickel concentrations above normal levels for drinking water, but no significant amount of copper was detected.

Treatment of effluents from dyeing units in Mali is not only a question of finding a chemical method. An infra-structure for treatment and an efficient implementation of laws concerning water quality, without threatening the livelihood for small scale dyers are as important aspects of the problem as the chemical ones.

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7 References

Aboulhassan M A, Souabi S, Yaacoubi A, Baudu M. (2005). Treatment of textile wastewater using a natural flocculant. *Environmental Technology* **26**:705-711.

Al Rmalli S W, Dahmani A A, Auein M M, Gleza A A. (2008) Biosorption of mercury from aqueous solutions by powdered leaves of castor tree (Ricinus communis L.). *Journal of Hazardous Materials* **152**: 955-959.

Amadou & Mariam. (2005). [CD]. *Dimanche à Bamako*. Nonesuch Records.

Armagan B, Özdemir O, Turan M, Celik M. (2003) Adsorption of negatively charged azo dyes onto surfactant-modified sepiolite. *Journal of Environmental Engineering* **129**(8): 709-715.

Attia A A, El-Hendawy A-N A, Khedr S A, El-Nabarawy T. (2004). *Adsorption Science & Technology* **22**(5): 411-426.

Chang R. (2005). *Chemistry, eighth edition*. McGraw Hill, New York.

Chern J-M, Huang S-N. (1998) Study of Nonlinear Wave Propagation Theory. 1 Dye Adsorption by Activated Carbon. *Industrial and Engineering Chemistry Research* **37**(1): 253-257.

Dali-Yousef Z, Bouabdasselem H, Bettahar N. (2006) Élimination des composés organiques par des argiles locales. *C. R. Chimie* **9**: 1295-1300.

Diarra M S. (2006). Dispositif de traitement des eaux usées de teinturerie chez ”Tantou Teinture” au Mali. *Info CREPA* N°52.

Dincer A R, Günes Y, Karakaya N, Günes E. (2007) Comparison of activated carbon and bottom ash for removal of reactive dye from aqueous solution. *Bioresource Technology* **98**:834-839.

Earth Trends (2003a). Water Resources and Freshwater Ecosystems-Mali. Earth Trends Country Profiles: http://earthtrends.wri.org/pdf_library/country_profiles/wat_cou_466.pdf. Avalil-able 2009-05-18.

Earth Trends (2003b). Water Resources and Freshwater Ecosystems-Sweden. Earth Trends Country Profiles: http://earthtrends.wri.org/pdf_library/country_profiles/wat_cou_752.pdf. Available 2009-05-18

El Zavahry M M, Kamel M M. (2004). Removal of azo and antharquinone dyes from aqueous solutions by Eichhornia Crassipes. *Water Research* **38**: 2967-2972.

European Commission (2003). *Integrated Pollution Prevention and Control (IPPC)*. Reference Document on Best Available Techniques for Textiles Industry.

Fatou N. (in prep). PhD thesis on decoloration of textile dyes by microorganisms. Faculté de Sciences et Techniques, Université de Bamako, Bamako.

Fofana M. (2009). Program Officer Natural Resources Management, Swedish International Develop-ment Cooperation (SIDA), Bamako. Personal communication. e-mail: mamby.fofana@sida.se

Gérimont P. (2008) *Teinturières à Bamako: Quand la couleur sort de sa réserve...* Ibis Press, Paris.

Ghebremichael K. (2004). *Moringa seed and pumice as alternative natural materials for drinking water treat-ment*. PhD thesis. Stockholm: KTH, Department of Land and Water Resources Engineering. TRITA-LWR PHD 1013

Gregory J, Duan J. (2001). Hydrolyzing metal salts as coagulants. *Pure Applied Chemistry* **73**:2017-2026.

Gupta V K, Ali I, Suhas, Mohan D. (2003) Equilibrium uptake and sorption dynamics for the removal of a basic dye (basic red) using low-cost adsorbents. *Journal of Colloid and Interface Science* **265**:257-264.

Harrelkas F, Azizi A, Yaacoubi A, Benhammou A, Noelle Pons M. (2009). Treatment of textile dye effluents using coagulation-flocculation coupled with membrane processes or adsorption on powdered activated carbon. *Desalination* **235**:330-339.

Ives K, Al Azharia Jahn, S. (2002). Coagulation and flocculation. In: Smet and van Wijk (Editors) *Small Community Water Supplies: Technology, people and partnership*. Technical paper no 40.

Lepinay G. (2008). *Proposition d'un système de prétraitement des effluents de teinture à Bamako (Mali)*. Rapport Licence professionelle – Option Gestion et Traitement des Sols et des Eaux. Université Catholique de l'Ouest, Angers.

Letterman R D, Amirtharajah A, O'Melia C R. (1999). Chapter 6: Coagulation and Flocculation. In: *Water Quality and Treatment-A Handbook of Community Water Supplies* (5th Edition). McGraw-Hill, New York.

Li K Y, Coe M T, Ramankutty N, De Jong R. (2007). Modeling the hydrological impact of land-use change in West Africa. *Journal of Hydrology* **337**:258-268

Lima E C, Royer B, Vaghetti J C P, Simon N W, da Cunha B M, Pavan F A, Benvenuti E V, Cataluna-Veses R, Arnold C. (2008) Application of Brazilian pine-fruit shell as a biosorbent to removal of reactive red 194 textile dye from aqueous solution. *Journal of Hazardous Materials* **155**(3): 536-550.

Mahmoodi N M, Arami M. (2008). Modelling and sensitivity analysis of dyes adsorption onto natural adsorbent from colored textile wastewater. *Journal of Applied Polymer Science* **109**:4043-4048.

Marobhe N J M. (2008). *Water supply in Tanzania and performance of local plant materials in purification of turbid water*. PhD thesis. Stockholm: KTH, Dept. of Land and Water Resources Engineering. ISSN 1650-8602.

Mathur N, Bhatnagar P, Nagar P, Bijarnia K. (2005). Mutagenicity assessment of effluents from textile/dye industries of Sanganer, Jaipur, India. *Ecotoxicology and Environmental Safety* **61**(1): 105-113.

McBride M B. (1994). *Environmental Chemistry of Soils*. Oxford University Press, New York.

McKay G. (1982). Adsorption of Dyestuffs from Aqueous Solutions with Activated Carbon I: Equilibrium and Batch Contact-Time Studies. *Journal of Chemical Technology and Biotechnology* **32**: 759-772.

Niger Basin Authority. (2001). *Africa Region - Reversing Land and Water Degradation Trends in the Niger River Basin*. Niamey, Niger. Report No. PID10632

Olivry J-C. (2005). *Niger River Basin: A Vision for Sustainable Management*. Herndon, VA, USA.

Orange D, Palangié A. (2006). Assessment of water pollution and risks to surface and groundwater resources in Bamako, Mali. In: Xu Y and Usher B. Ed. *Groundwater Pollution in Africa*. Taylor & Francis Group, London.

Pala A, Tokat E. (2002). Color removal from cotton textile industry wastewater in an activated sludge system with various additives. *Water Research* **36**:2920-2925.

Papić S, Koprivanac N, Lončarić Božić A, Meteš A. (2004). Removal of some reactive dyes from synthetic wastewater by combined Al(III) coagulation/carbon adsorption process. *Dyes and Pigments* **62**:291-298.

Plea M. (2009). Professor Faculté des Sciences et Techniques, Université de Bamako, Bamako. Personal communication. e-mail: mamaplea@yahoo.fr

République du Mali (2002). *Code de l'eau loi n°02-006/du 31 janvier 2002*. Journal officiel de la republique du Mali, Quarantième Année Special n°8 02 Mai 2002. Secretariat general du gouvernement.

République du Mali (2005). Carte Touristique du Mali. Institut Geographique du Mali/Office Malien du Tourisme et de l'Hôtellerie, Bamako.

République du Mali (2006). *Growth and Poverty Reduction Strategy Paper, 2nd Generation PRSP 2007-2011*. Ministère d'Economie et de Finance.

République du Mali (2007). *Statistique du commerce exterieur du Mali, Bulletin Annuel 2006*. Ministère du Plan et de l'Amenagement du Territoire/Direction Nationale de la Statistique et de l'Informatique.

Roquin C, Freyssinet PH, Zeegers H, Tardy Y. (1990). Element distribution patterns in laterites of southern Mali: consequence for geochemical prospecting and mineral exploration. *Applied Geochemistry* **5**:303-315.

Sajidu S M I. (2007). E*valuation of Water/Wastewater Quality In Blantyre City and Heavy Metal Removing using Alkaline Clays and Moringa Seeds*. PhD Thesis, Chemistry Department, University of Malawi.

Skyddshandbok 1 kemiska ämnen. (1979). Arbetarskyddsstyrelsen.

Snoeyink V L, Summers R S. (1999). Chapter 13: Adsorption of organic compounds. In: *Water Quality and Treatment-A Handbook of Community Water Supplies* (5th Edition). McGraw-Hill.

Sposito G. (1989). Chapter 10: Soil Colloidal Phenomena. In: *The Chemistry of Soils*. Oxford University Press, Oxford.

Sulak M T, Demirbas E, Kobya M. (2007). Removal of Astrazon Yellow 7GL from aqueous solutions by adsorption onto wheat bran. *Bioresource Technology* **98**:2590-2598.

Sutherland J P, Folkard G K, Mtawali M A, Grant W D. (1994). Moringa oleifera as a natural coagulant. 20th WEDC Conference, Affordable Water supply and Sanitation, Colombo Sri Lanka, pp. 297-299

Sällström M. (2008). *Physico-chemical characteristics of some soils from Mali and their potential in heavy metal removal*. Uppsala: Sveriges lantbruksuniversitet, Institutionen för markvetenskap, avdelningen för markkemi och jordmånslära. Examens- och seminariearbeten Nr 92 ISSN 1102-1381

Tahir H, Sultan M, Jahanzeb Q. (2008). Removal of basic dye methylen blue by using biosorbents Ulva lactuca and Sargassum. *African Journal of Biotechnology* **7**(15): 2549-2655.

Traoré A Z, Bokar H, Traoré D, Diakite L. (2006). Statistical assessment of groundwater quality in Bamako City, Mali. In: Xu Y and Usher B. Ed. *Groundwater Pollution in Africa*. Taylor & Francis Group, London.

UNDP (2006). Human Development Report 2006: *Beyond scarcity: Power, poverty and the global water crisis*. United Nations Development Programme: New York.

UNDP (2007) Human Development Report 2007/2008: *Fighting climate change: Human solidarity in a divided world*. United Nations Development Programme: New York.

UNEP/IISD (International Institute for Sustainable Development) (2005). Connecting poverty & ecosystem services. A series of seven sountry scoping studies. Focus on Mali. 29 p.

UNEP (2008). *Africa : Atlas of Our Changing Environment*. Division of Early Warning and Assessmen (DEWA) United Nations Environment Programme (UNEP). Nairobi.

UNESCO (2006). *Rapport national sur la mise en valeur des ressources en eau : Mali*. Programme mondiale pour l'evaluation des ressources en eau.

USEPA (1996). *Manual Best Management Practices for Pollution Prevention in the Textile Industry*. Cincinnatti: United States Environmental Protection Agency. EPA/625/R-96/004.

USHHS (2007). *Toxicological profile for barium and barium compounds*. United States Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry.

Vandevivere P C, Bianchi R, Verstraete W. (1998). Treatment and Reuse of Wastewater from the Textile Wet-Processing Industry : Review of Emerging Technologies. *Journal of Chemical Technology and Biotechnology* **72** :289-302.

Venkata Mohan S, Chandrasekhar Rao N, Karthikeyan J. (2002). Adsorptive removal of direct azo dye from aqueous phase onto coal based sorbents: a kinetic and mechanistic study. *Journal of Hazardous Materials* **B90**: 189-204.

WHO (2003). *Zinc in Drinking-water. Background document for development of WHO guidelines for Drinking-water Quality*. WHO/SDE/WSH/03.04/17.

WHO (2004). *Barium in Drinking-water. Background document for development of WHO guidelines for Drinking-water Quality*. WHO/SDE/WSH/03.04/76

WHO (2005). *Nickel in Drinking-water. Background document for development of WHO guidelines for Drinking-water Quality*. WHO/SDE/WSH/05.08/55.

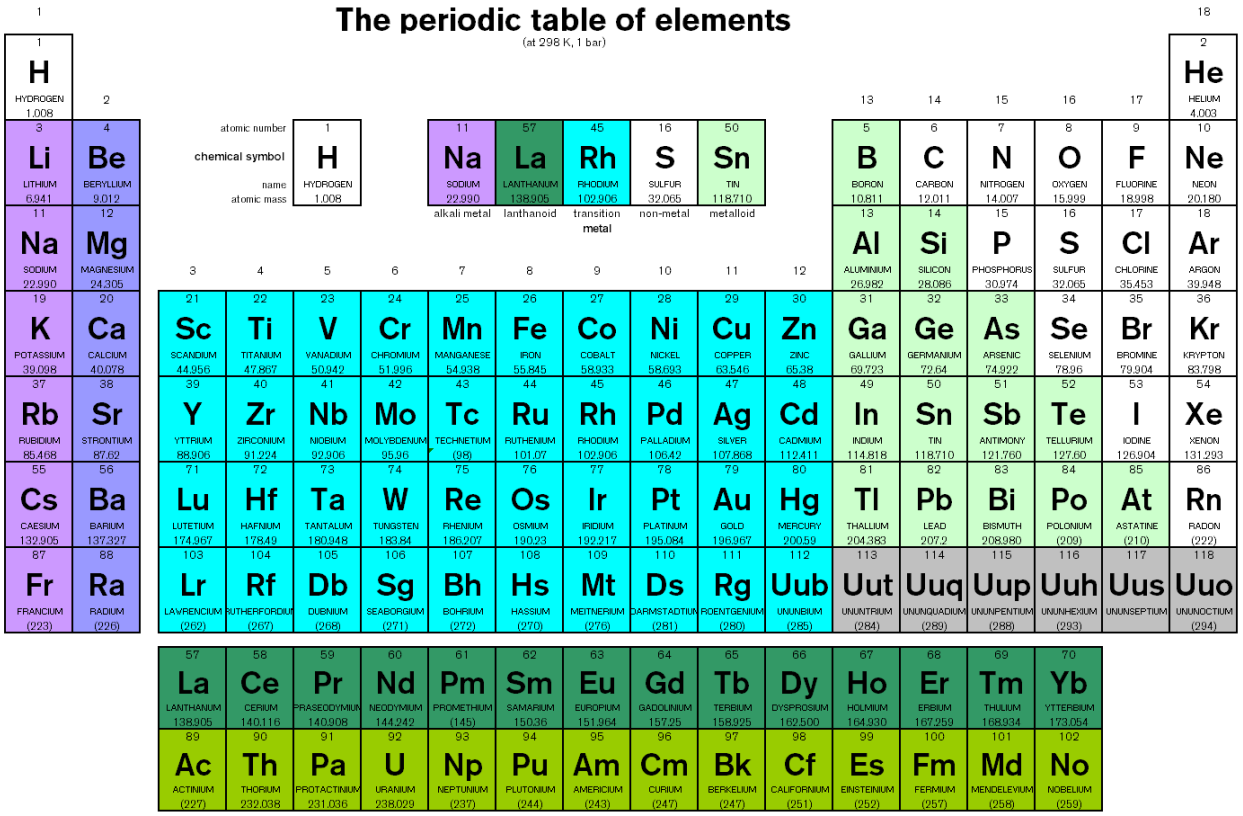
Yeh R Y L, Thomas A. (1995). Color-difference measurement and color removal from dye wastewaters using different adsorbents. *Journal of Chemical Technology and Biotechnology* **63**(1): 55-59

Zahn S L, Lin J X, Fang M H, Qian X Q. (2008). Adsorption of anionic dye by magnesium hydroxide-modified diatomite. Rare Metal Materials and Engineering 37 (Suppl. 2): 644-647.

Zollinger H. (1991). *Color Chemistry. Syntheses, Properties and Applications of Organic Dyes and Pigments*. VCH Weinheim. Second edition.

Özdemir O, Armagan B, Turan M, Celik M S. (2004). Comparison of the adsorption characteristics of azo-reactive dyes on mezoporous minerals. *Dyes and Pigments* **62**: 49-60.

APPENDIX 1


The periodic table of elements
(at 298 K, 1 bar)
atomic number
chemical symbol
name
atomic mass
alkali metal
lanthanoid
transition metal
non-metal
metalloid

APPENDIX 2

Raw data from jar tests with diluted effluents from Badalabougou. Difference refers to the result of the subtraction after-before jar test.

A) Jar test 1. Materials added:

	Amount added to 800 ml	Concnetration in solution added
Bentonite	4.05 g	
PAC	4.00 g	
Rice bran	4.06 g	
$Al_2(SO_4)^3$	4.8 ml	50 g l^{-1}
$FeCl_3$	4.8 ml	50 g l^{-1}

	pH	temperature [°C]	conductivity [mS cm^{-1}]	TDS [mg l^{-1}]	turbidity [FTU]	DO [mg l^{-1}]
Before jar test						
Bentonite	11.64	29.6	3.12	1456	36.1	5.1
PAC	11.73	29.1	3.14	1478	35.4	5.2
Rice bran	11.76	29.1	3.11	1470	36.4	5.2
$Al_2(SO_4)^3$	11.75	28.9	3.11	1471	35.9	4.9
$FeCl_3$	11.78	29.0	3.11	1470	35.5	5.0
Blank	11.79	28.9	3.09	1462	35.8	5.2
After jar test						
Bentonite	10.24	29.9	2.02	919	93.4	4.3
PAC	11.74	29.4	3.07	1434	27.9	5.0
Rice bran	11.65	29.4	2.77	1290	330	4.0
$Al_2(SO_4)^3$	11.56	29.3	2.68	1248	37.3	6.0
$FeCl_3$	2.00	29.4	7.42	3570	6.90	6.6
Blank	11.66	29.5	3.08	1436	37.4	5.4
Difference						
Bentonite	-1.4	0.3	-1.1	-537	57.3	-0.8
PAC	0.01	0.3	-0.07	-44	-7.5	-0.2
Rice bran	-0.11	0.3	-0.34	-180	293.6	-1,2
$Al_2(SO_4)^3$	-0.19	0.4	-0.43	-223	1.4	1.1
$FeCl_3$	-9.78	0.4	4.31	2100	-28.6	1.6
Blank	-0.13	0.6	-0.01	-26	1.6	0.2

B) Jar test 2. Materials added:

	Amount added to 800 ml	Concnetration in solution added
Bentonite	6.41 g	
PAC	6.44 g	
Rice bran	6.40 g	
$Al_2(SO_4)^3$	8 ml	50 g l^{-1}
$FeCl_3$	8 ml	50 g l^{-1}

	pH	temperature [°C]	conductivity [mS cm^{-1}]	TDS [mg l^{-1}]	turbidity [FTU]	DO [mg l^{-1}]
Before jar test						
Bentonite	11.87	28.3	3.10	1486	37.1	4.5
PAC	11.89	28.3	3.14	1504	37.0	4.7
Rice bran	11.91	28.3	3.12	1496	37.1	4.9
$Al_2(SO_4)^3$	11.92	28.3	3.11	1490	37.1	5.1
$FeCl_3$	11.95	28.3	3.12	1493	37.1	4.6
Blank	11.92	28.7	314	1495	36.4	5.0
After jar test						
Bentonite	10.06	30.1	2.03	919	129	4.0
PAC	11.85	29.6	3.07	1429	44.5	4.7
Rice bran	11.67	29.7	2.60	1197	322	3.6
$Al_2(SO_4)^3$	11.48	29.6	2.46	1134	39.5	5.1
$FeCl_3$	1.82	30.6	10.44	5090	7.34	5.5
Blank	11.95	29.9	3.12	1444	37.8	5.7
Difference						
Bentonite	-1.81	1.8	-1.07	-567	91.9	-0.5
PAC	-0.04	1.3	-0.07	-75	7.50	0.0
Rice bran	-0.24	1.4	-0.52	-299	285	-1.3
$Al_2(SO_4)^3$	-0.44	1.3	-0.65	-356	2.40	0.0
$FeCl_3$	-10.13	2.3	7.32	3597	-29.8	0.9
Blank	0.03	1.2	-0.02	-51	1.40	0.7

APPENDIX 3

Raw data from jar tests with diluted effluents from Badalabougou with adjusted pH. Difference refers to the result of the subtraction after-before jar test.

Jar test 3. Materials added:

	Amount added to 800 ml	**Concnetration in solution added**
Bentonite	6.39 g	
PAC	6.40 g	
Rice bran	6.43 g	
$Al_2(SO_4)^3$	8 ml	50 g l^{-1}
$FeCl_3$	8 ml	50 g l^{-1}

	pH	**temperature** [°C]	**conductivity** [mS cm^{-1}]	**TDS** [mg l^{-1}]	**turbidity** [FTU]	**DO** [mg l^{-1}]
Before jar test						
Bentonite	8.66	29.7	2.16	993	41.6	3.1
PAC	8.59	29.3	2.16	999	40.2	3.5
Rice bran	8.51	29.4	2.17	1003	40.6	3.0
$Al_2(SO_4)^3$	8.44	29.1	2.16	999	40.3	3.2
$FeCl_3$	8.44	29.2	2.18	1010	41.8	2.5
Blank	8.42	29.2	2.19	1015	41.7	2.5
After jar test						
Bentonite	6.8	30.4	2.50	1139	125	3.4
PAC	9.95	29.8	2.25	1029	25.7	3.1
Rice bran	7.95	30.0	2.24	1024	237	3.1
$Al_2(SO_4)^3$	6.42	29.8	2.21	1009	72.9	4.6
$FeCl_3$	1.81	30.0	11.34	5560	12.10	5.0
Blank	8.42	30.1	2.25	1022	42.1	3.3
Difference						
Bentonite	-1.86	0.7	0.34	146	83.4	0.3
PAC	1.36	0.5	0.09	30	-14.5	-0.4
Rice bran	-0.56	0.6	0.07	21	196.4	0.1
$Al_2(SO_4)^3$	-2.02	0.7	0.05	10	32.6	1.4
$FeCl_3$	-6.63	0.8	9.16	4550	-29.7	2.5
Blank	0.00	0.9	0.06	7	0.4	0.8

APPENDIX 4

Raw data from jar tests with diluted effluents from Badalabougou. Performance of GAC for different pH values was tested. Difference refers to the result of the subtraction after-before jar test.

Jar test 4. Materials added:

	Amount GAC added to 800 ml
pH 10	4.05 g
pH 8	4.02 g
pH 6	4.00 g
pH 4	4.01 g

	pH	**temperature** [°C]	**conductivity** [mS cm^{-1}]	**TDS** [mg l^{-1}]	**turbidity** [FTU]	**DO** [mg l^{-1}]
Before jar test						
pH 10	9.81	29.2	2.07	954	37.9	4.1
pH 8	7.90	29.2	2.08	963	39.9	2.2
pH 6	6.04	29.2	2.05	947	42.7	4.6
pH 4	4.22	29.4	2.09	964	44.5	5.8
Blank	11.78	29.4	3.04	1426	37.4	5.1
After jar test						
pH 10	9.72	29.0	2.20	1022	36.8	3.7
pH 8	8.81	28.9	2.23	1036	37.7	3.2
pH 6	6.68	29.0	2.24	1040	40.6	3.5
pH 4	6.22	29.1	2.27	1056	42.2	4.4
Blank	11.36	29.4	2.57	1191	37.8	5.3
Difference						
pH 10	-0.09	-0.2	0.13	68	-1.1	-0.4
pH 8	0.91	-0.3	0.15	73	-2.2	1.0
pH 6	0.64	-0.2	0.19	93	-2.1	-1.1
pH 4	2.00	-0.3	0.18	92	-2.3	-1.4
Blank	-0.42	0.0	-0.47	-235	0.4	0.2

APPENDIX 5

Raw data from jar tests with diluted effluents from Ouolofobougou. Difference refers to the result of the subtraction after-before jar test.

Jar test 5. Materials added:

	Amount added to 800 ml
PAC dilution 100	8.02 g
PAC dilution 50	8.01 g
GAC	8.01 g
Rice chaff	4.00 g
Rice chaff	8.03 g

	pH	**temperature** [°C]	**conductivity** [mS cm^{-1}]	**TDS** [mg l^{-1}]	**turbidity** [FTU]	**DO** [mg l^{-1}]
Before jar test						
PAC dilution 100	6.90	30.4	110	47	5.75	5.4
PAC dilution 50	6.84	30.2	220	95	8.03	5.1
GAC	6.66	30.3	220	95	7.70	5.3
Rice chaff	6.68	30.1	219	95	7.63	5.3
Rice chaff	6.89	30.2	221	95	7.48	5.3
Temoine	6.86	30.1	220	95	7.59	6.1
After jar test						
PAC dilution 100	9.55	30.5	228	98	49.7	6.0
PAC dilution 50	9.52	30.2	333	144	70.0	5.5
GAC	9.40	30.0	436	191	28.5	4.7
Rice chaff	7.01	30.2	276	119	13.4	4.6
Rice chaff	6.69	30.1	314	136	18.1	4.0
Temoine	6.93	30.5	225	97	7.59	5.3
Difference						
PAC dilution 100	2.65	0.1	118	51	43.9	0.6
PAC dilution 50	2.68	0.0	113	50	62.0	0.4
GAC	2.74	-0.3	216	96	20.8	-0.6
Rice chaff	0.33	0.1	57	24	5.8	-0.7
Rice chaff	-0.20	-0.1	93	41	10.7	-1.3
Temoine	0.07	0.4	5	2.0	0.0	-0.8

Jar test 6. Materials added:

	Amount added to 800 ml
Laterite 250 µm	4.00 g
Laterite 250 µm	8.03 g
Laterite 800 µm	4.01 g
Laterite 800 µm	8.02 g
Laterite 800 µm	8.01 g

	pH	temperature [°C]	conductivity [mS cm^{-1}]	TDS [mg l^{-1}]	turbidity [FTU]	DO [mg l^{-1}]
Before jar test						
Laterite 250 µm 5 g l^{-1} effluent diluted 50	6.66	27.9	253	114	7	5.8
Laterite 250 µm 10 g l^{-1} effluent diluted 50	6.73	28.5	252	113	7	5.7
Laterite 800 µm 5 g l^{-1} effluent diluted 50	6.65	27.6	250	114	7	5.8
Laterite 800 µm 10 g l^{-1} effluent diluted 50	6.65	27.6	249	114	7	5.6
Laterite 800 µm 10 g l^{-1} distilled water	5.79	28.0	25,7	11	1	5.9
Blank effluent diluted 50	6.67	27.5	250	114	7	5.6
After jar test						
Laterite 250 µm 5 g l^{-1} effluent diluted 50	6.95	28.5	230	103	231	5.0
Laterite 250 µm 10 g l^{-1} effluent diluted 50	6.65	28.4	251	113	484	5.0
Laterite 800 µm 5 g l^{-1} effluent diluted 50	6.78	28.1	256	116	208	5.0
Laterite 800 µm 10 g l^{-1} effluent diluted 50	6.69	28.2	249	112	501	4.7
Laterite 800 µm 10 g l^{-1} distilled water	6.35	28.1	17.9	8	344	5.8
Blank effluent diluted 50	6.82	28.2	251	113	7	5.0
Difference						
Laterite 250 µm 5 g l^{-1} effluent diluted 50	0.29	0.6	-23	-11	224	-0.8
Laterite 250 µm 10 g l^{-1} effluent diluted 50	-0.08	-0.1	-1.0	0	477	-0.7
Laterite 800 µm 5 g l^{-1} effluent diluted 50	0.13	0.5	6.0	2	201	-0.8
Laterite 800 µm 10 g l^{-1} effluent diluted 50	0.04	0.6	0.0	-2	494	-0.9
Laterite 800 µm 10 g l^{-1} distilled water	0.56	0.1	-7.8	-4	343	-0.1
Blank effluent diluted 50	0.15	0.7	1.0	-1	0	-0.6

Jar test 7. Materials added:

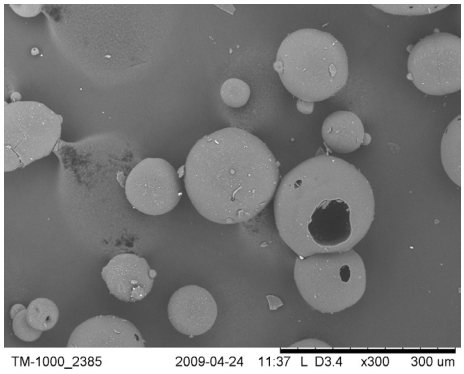
	Amount added to 800 ml
Rice chaff grained 800 µm	4.02 g
Rice chaff grained 800 µm	8.03 g
Rice chaff grained 800 µm	8.00 g
Rice chaff grained 800 µm	8.01 g
PAC	8.00 g
GAC	8.03 g

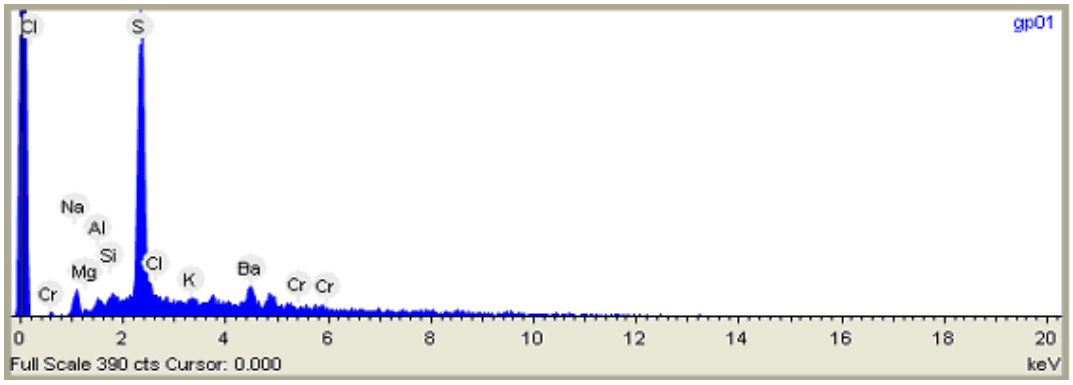
	pH	**temperature** [°C]	**conductivity** [mS cm^{-1}]	**TDS** [mg l^{-1}]	**turbidity** [FTU]	**DO** [mg l^{-1}]
Before jar test						
Rice chaff grained 800 µm 5 g l^{-1} effluent diluted 50	6.82	27.9	227	103	7.1	6.0
Rice chaff grained 800 µm 10 g l^{-1} effluent diluted 50	6.58	27.9	219	99	6.7	6.3
Rice chaff grained 800 µm 10 g l^{-1} distilled water	5.79	28.0	26	11	1.0	5.9
Rice chaff grained 800 µm 10 g l^{-1} distilled water	5.79	28.0	26	11	1.0	5.9
PAC 10 g l^{-1} distilled water	5.79	28.0	26	11	1.0	5.9
GAC 10 g l^{-1} distilled water	5.79	28.0	26	11	1.0	5.9
After jar test						
Rice chaff grained 800 µm 5 g l^{-1} effluent diluted 50	6.22	28.9	289	129	27.0	1.8
Rice chaff grained 800 µm 10 g l^{-1} effluent diluted 50	5.84	28.7	347	155	43.8	1.0
Rice chaff grained 800 µm 10 g l^{-1} distilled water	5.46	28.6	143	64	36.0	1.8
Rice chaff grained 10 g l^{-1} distilled water	5.57	27.5	135	61	15.4	2.0
PAC 10 g l^{-1} distilled water	8.06	27.5	147	66	12.4	5.9
GAC 10 g l^{-1} distilled water	8.72	27.9	232	105	6.2	5.7
Difference						
Rice chaff grained 800 µm 5 g l^{-1} effluent diluted 50	-0.60	1.0	62	26	19.9	-4.2
Rice chaff grained 800 µm 10 g l^{-1} effluent diluted 50	-0.74	0.8	128	56	37.1	-5.3
Rice chaff grained 800 µm 10 g l^{-1} distilled water	-0.33	0.6	117	52	35.1	-4.1
Rice chaff grained 10 g l^{-1} distilled water	-0.22	-0.5	109	50	14.4	-3.9
PAC 10 g l^{-1} distilled water	2.27	-0.5	121	55	11.4	0.0
GAC 10 g l^{-1} distilled water	2.93	-0.1	206	94	5.2	-0.2

APPENDIX 6

Results from SEM analyses of green dyestuff.

A)





Acquisition conditions

Acquisition time (s)	60.0
Process time	4
Accelerating voltage (kV)	15.0

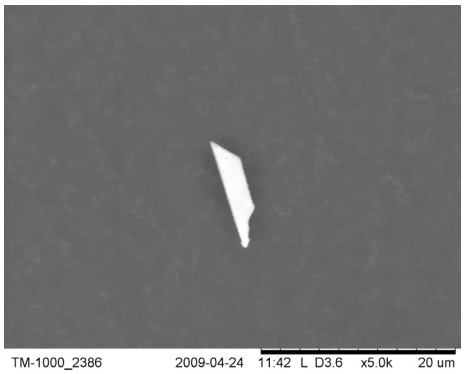
Quantification Settings

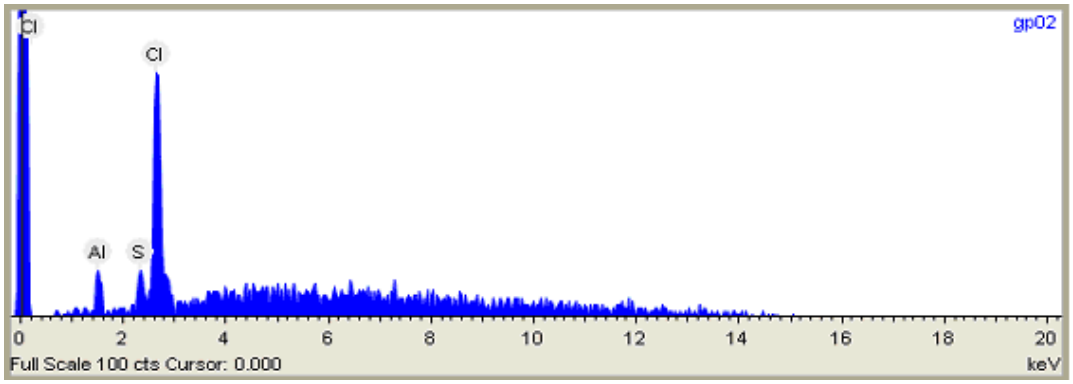
Quantification method	All elements (normalised)

Summary results

Element	Weight %
Sodium	8.3
Magnesium	0.7
Aluminum	1.8
Silicon	1.9
Sulfur	56.5
Chlorine	1.4
Potassium	1.4
Chromium	1.0
Barium	27.1

B)





Acquisition conditions

Acquisition time (s)	60.0
Process time	4
Accelerating voltage (kV)	15.0

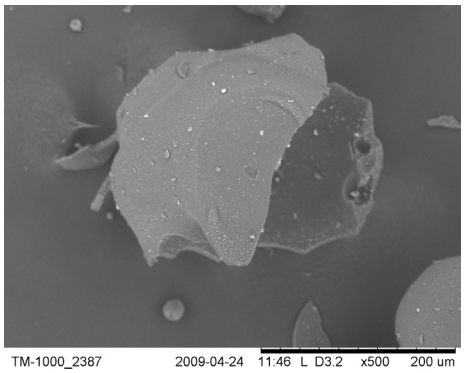
Quantification Settings

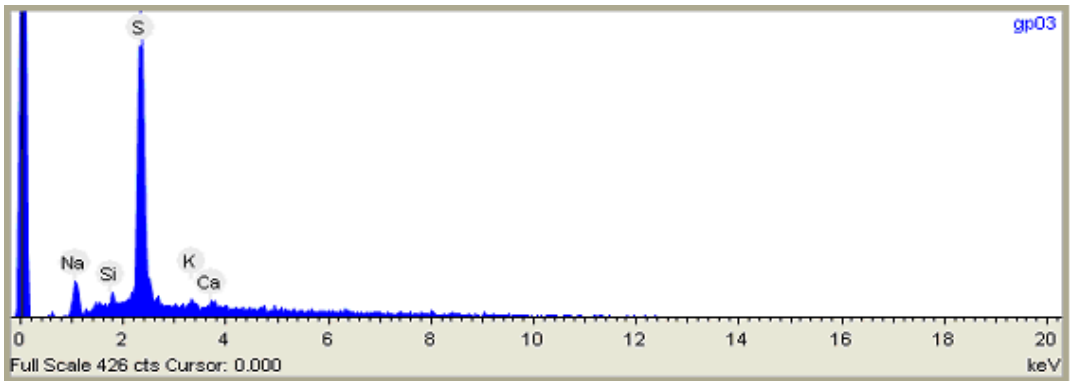
Quantification method	All elements (normalised)

Summary results

Element	Weight %
Aluminum	9.1
Sulfur	8.5
Chlorine	82.4

C) Light area





Acquisition conditions

Acquisition time (s)	60.0
Process time	4
Accelerating voltage (kV)	15.0

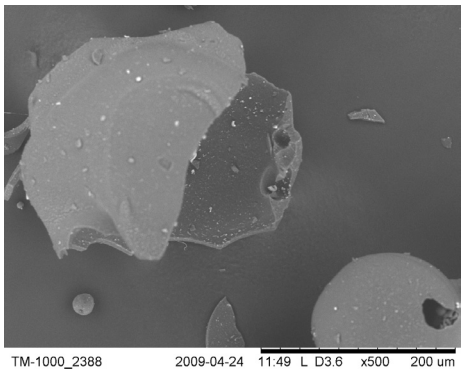
Quantification Settings

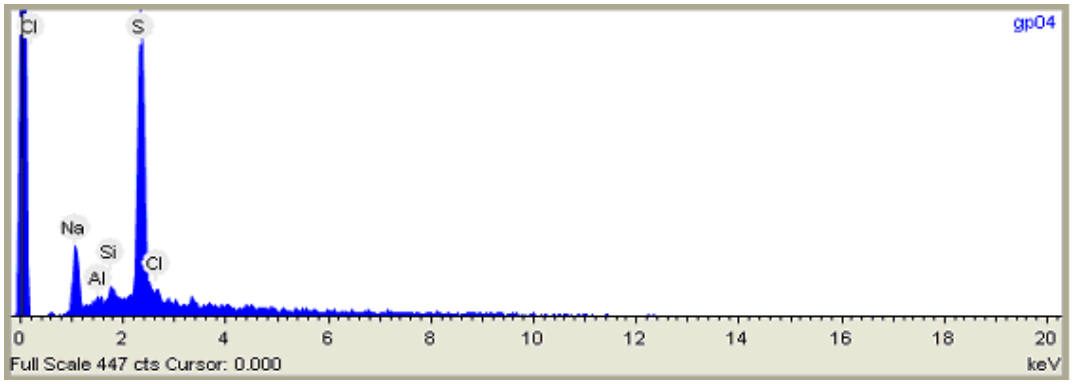
Quantification method	All elements (normalised)

Summary results

Element	Weight %
Sodium	14.2
Silicon	1.8
Sulfur	78.1
Potassium	3.4
Calcium	2.6

D) Dark area





Acquisition conditions

Acquisition time (s)	60.0
Process time	4
Accelerating voltage (kV)	15.0

Quantification Settings

Quantification method	All elements (normalised)

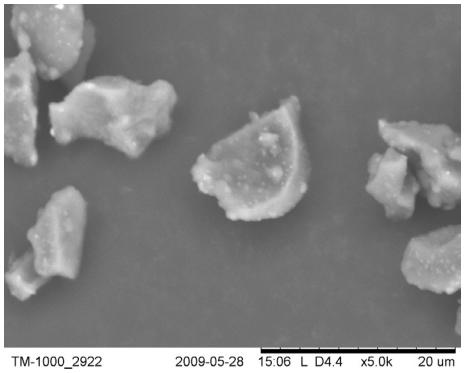
Summary results

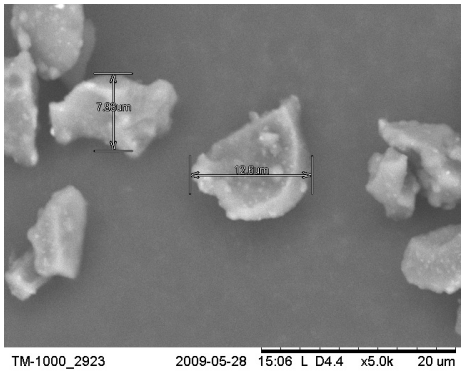
Element	Weight %
Sodium	22.4
Aluminum	1.2
Silicon	2.7
Sulfur	69.0
Chlorine	4.7

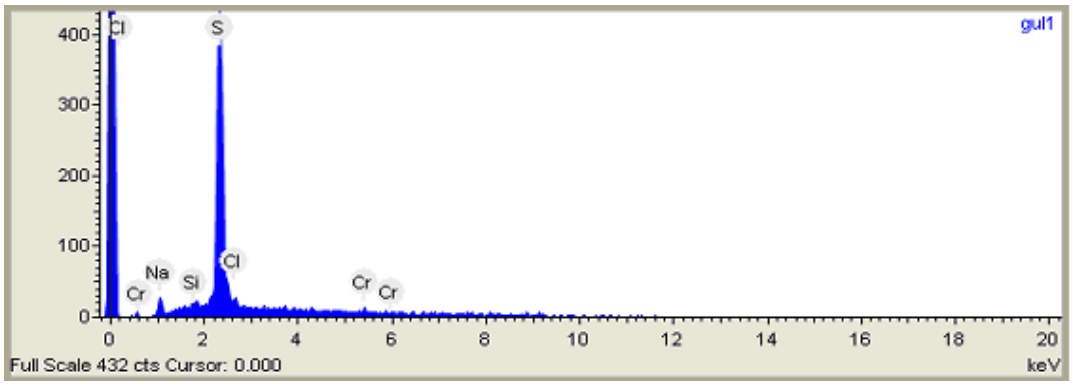
APPENDIX 7

Results from SEM analyses of yellow dyestuff.

A)







Acquisition conditions

Acquisition time (s)	60.0
Process time	4
Accelerating voltage (kV)	15.0

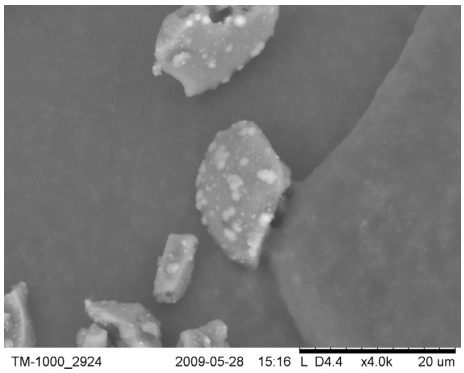
Quantification Settings

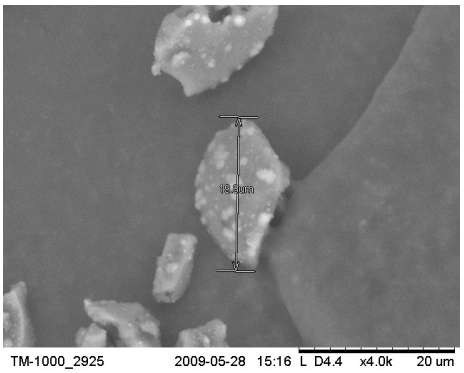
Quantification method	All elements (normalised)

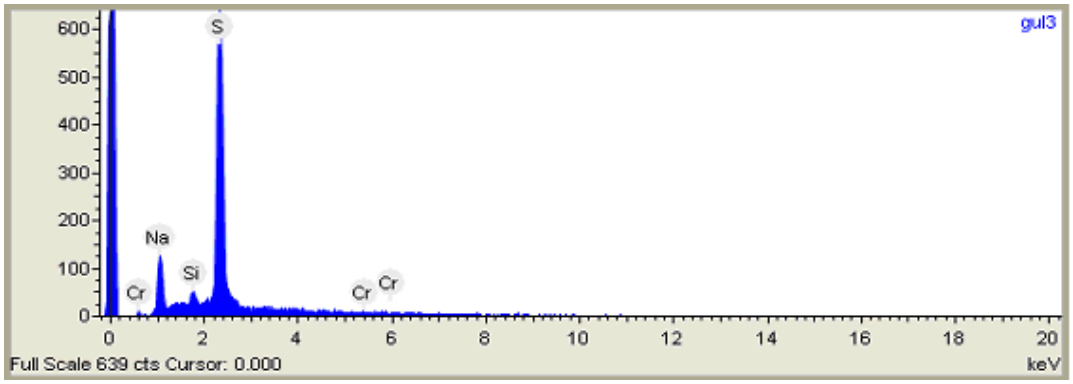
Summary results

Element	Weight %
Sodium	7.6
Silicon	0.8
Sulfur	84.8
Chlorine	4.9
Chromium	1.8

B)







Acquisition conditions

Acquisition time (s)	60.0
Process time	4
Accelerating voltage (kV)	15.0

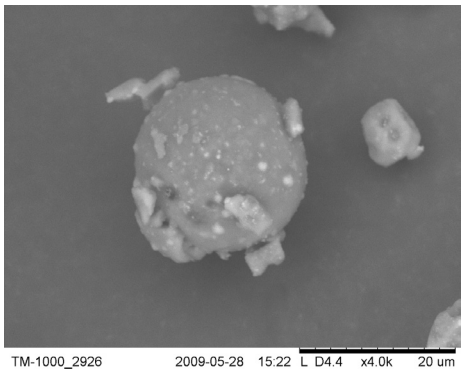
Quantification Settings

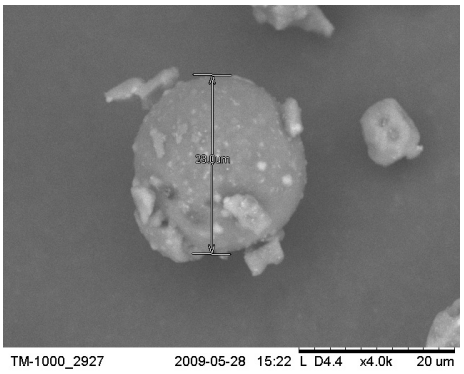
Quantification method	All elements (normalised)

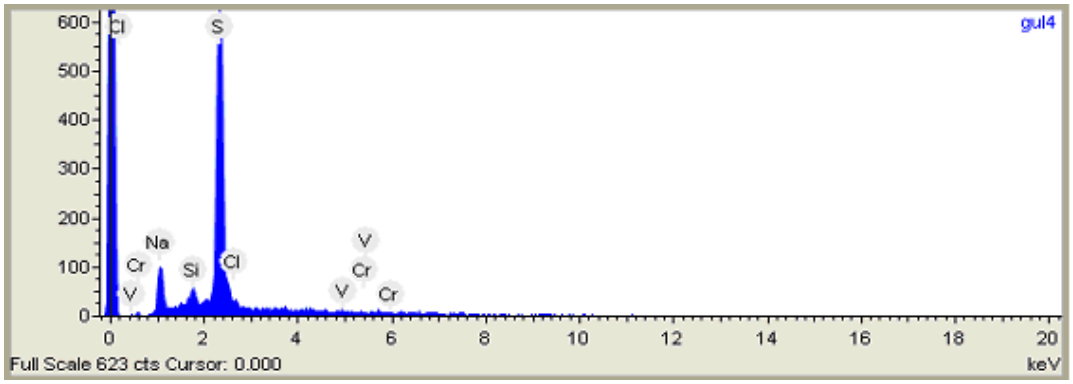
Summary results

Element	Weight %
Sodium	21.6
Silicon	2.8
Sulfur	75.3
Chromium	0.3

C)







Acquisition conditions

Acquisition time (s)	60.0
Process time	4
Accelerating voltage (kV)	15.0

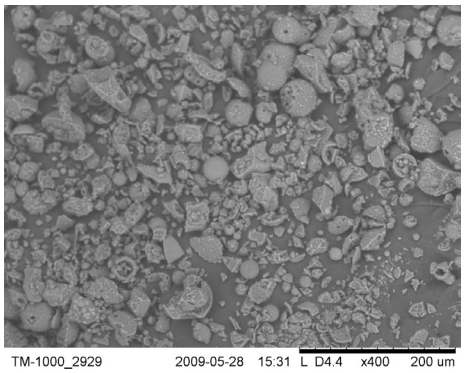
Quantification Settings

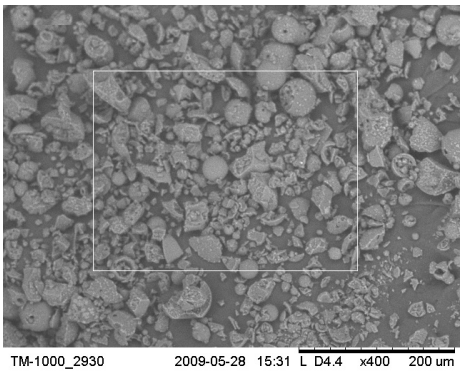
Quantification method	All elements (normalised)

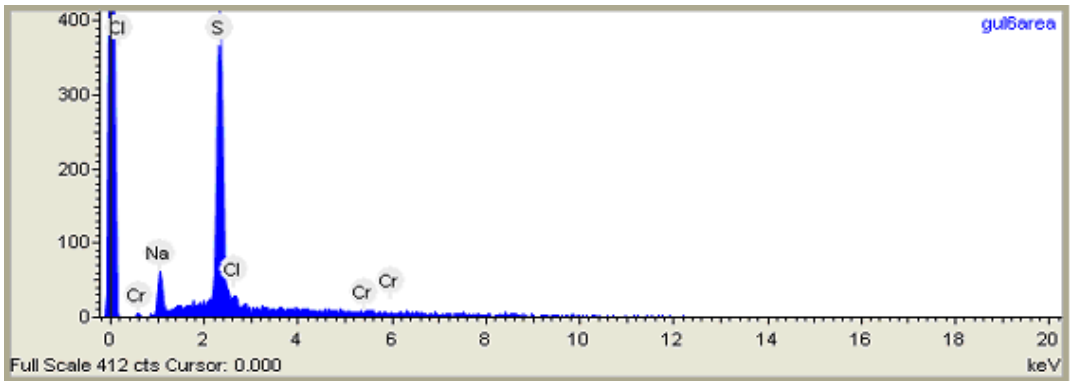
Summary results

Element	Weight %
Sodium	17.8
Silicon	2.7
Sulfur	77.2
Chlorine	2.1
Vanadium	0.2
Chromium	0.0

D)







Acquisition conditions

Acquisition time (s)	60.0
Process time	4
Accelerating voltage (kV)	15.0

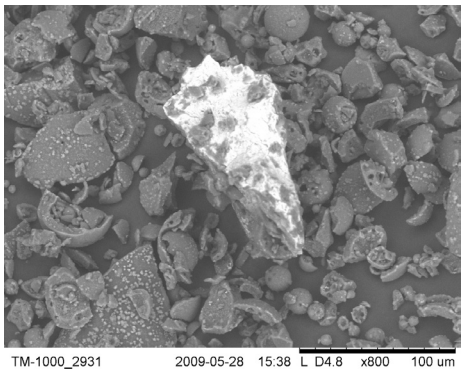
Quantification Settings

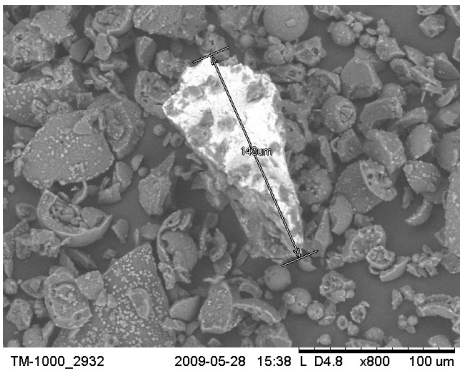
Quantification method	All elements (normalised)

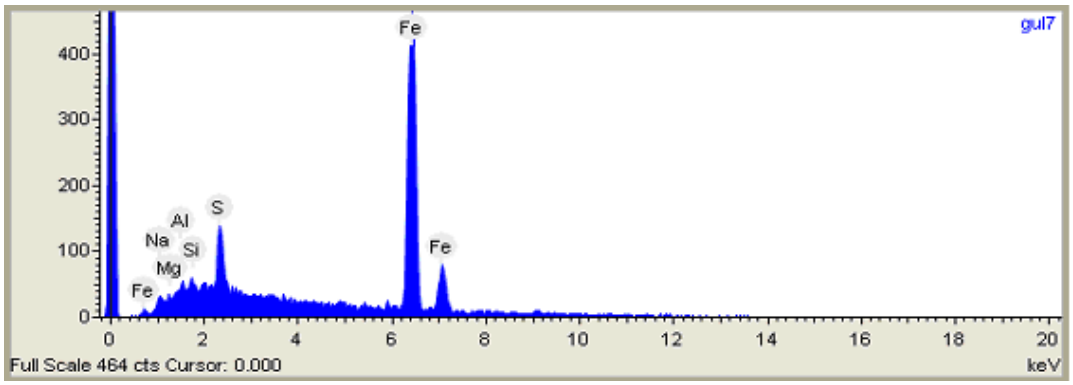
Summary results

Element	Weight %
Sodium	18.3
Sulfur	74.7
Chlorine	7.0
Chromium	0.0

E)







Acquisition conditions

Acquisition time (s)	60.0
Process time	4
Accelerating voltage (kV)	15.0

Quantification Settings

Quantification method	All elements (normalised)

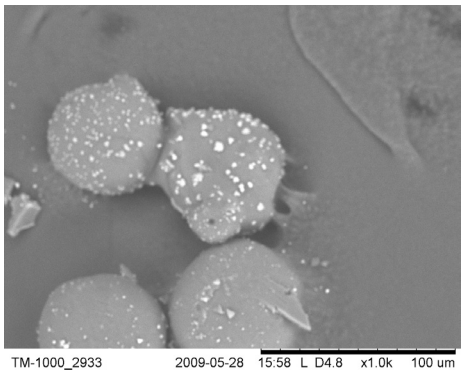
Summary results

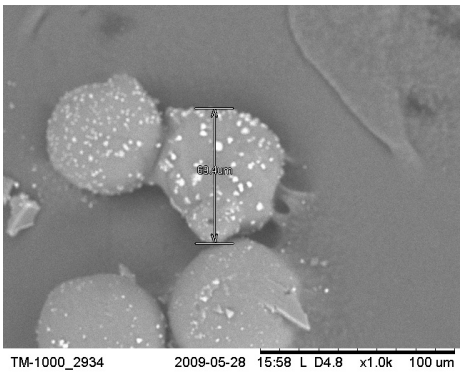
Element	Weight %
Sodium	2.9
Magnesium	0.2
Aluminum	0.3
Silicon	0.7
Sulfur	4.0
Iron	91.9

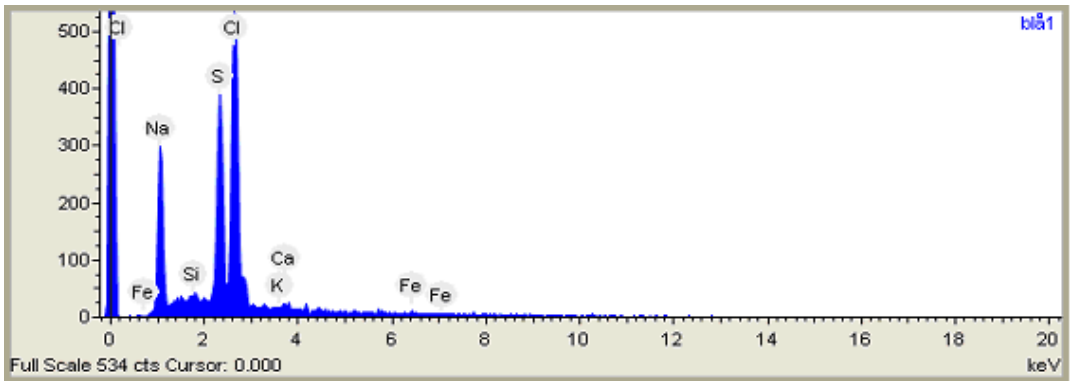
APPENDIX 8

Results from SEM analyses of blue dyestuff.

A)







Acquisition conditions

Acquisition time (s)	60.0
Process time	4
Accelerating voltage (kV)	15.0

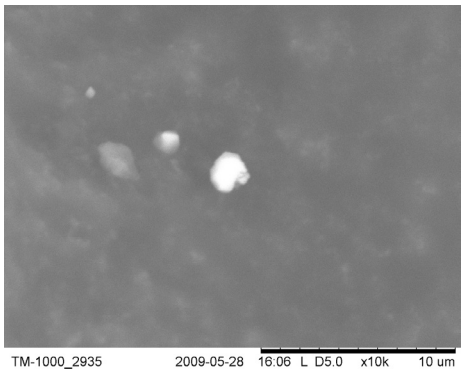
Quantification Settings

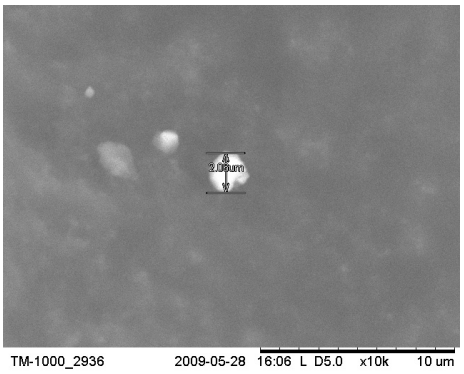
Quantification method	All elements (normalised)

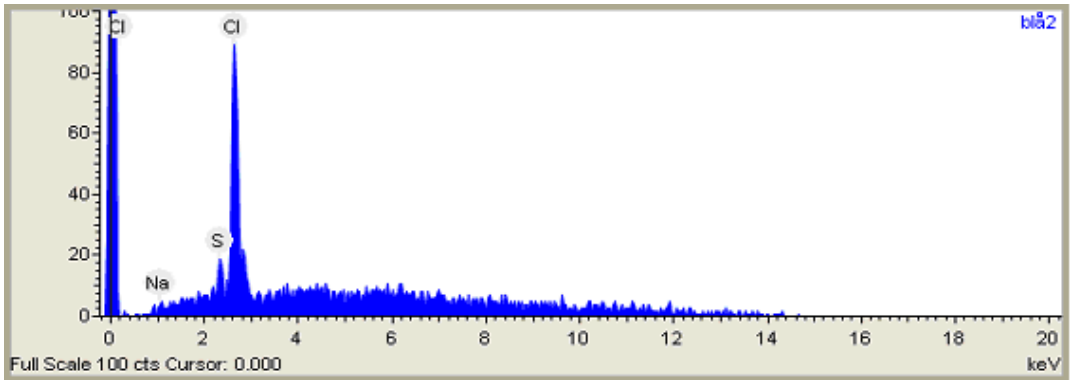
Summary results

Element	Weight %
Sodium	29.3
Silicon	0.5
Sulfur	22.9
Chlorine	45.4
Potassium	0.0
Calcium	0.8
Iron	1.0

B)







Acquisition conditions

Acquisition time (s)	60.0
Process time	4
Accelerating voltage (kV)	15.0

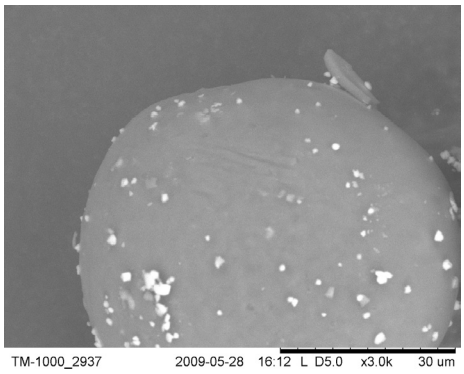
Quantification Settings

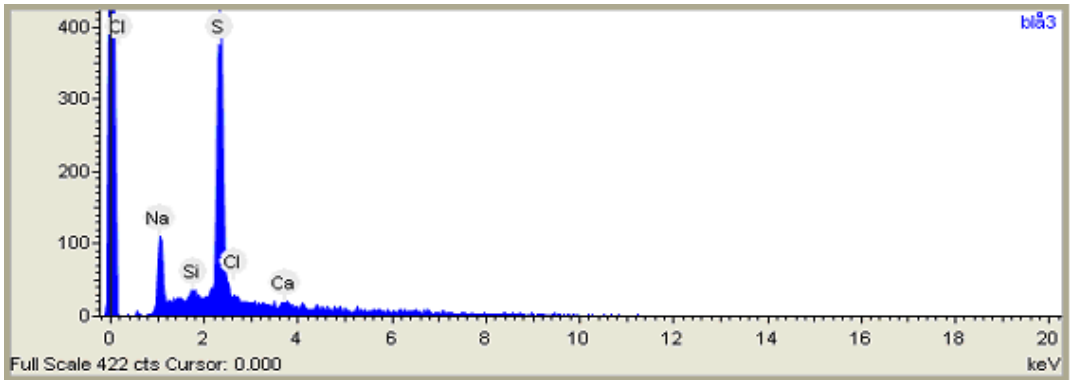
Quantification method	All elements (normalised)

Summary results

Element	Weight %
Sodium	1.7
Sulfur	8.6
Chlorine	89.7

C)





Acquisition conditions

Acquisition time (s)	60.0
Process time	4
Accelerating voltage (kV)	15.0

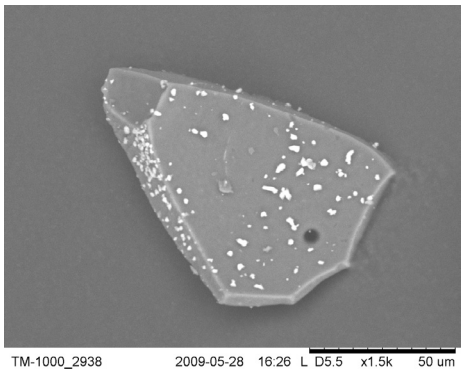
Quantification Settings

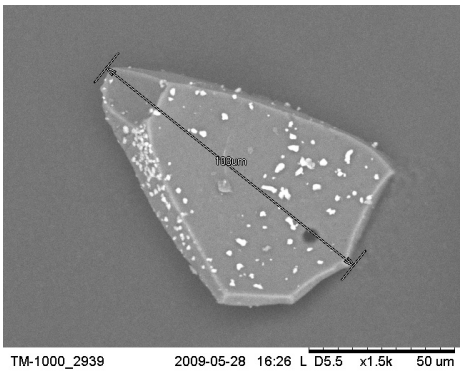
Quantification method	All elements (normalised)

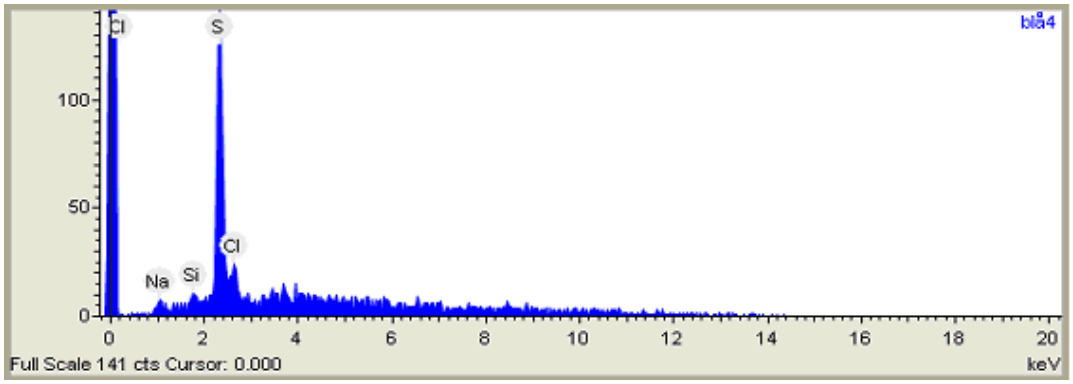
Summary results

Element	Weight %
Sodium	26.8
Silicon	1.4
Sulfur	66.9
Chlorine	3.4
Calcium	1.6

D)







Acquisition conditions

Acquisition time (s)	60.0
Process time	4
Accelerating voltage (kV)	15.0

Quantification Settings

Quantification method	All elements (normalised)

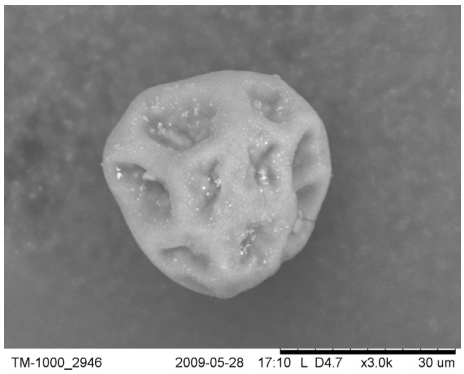
Summary results

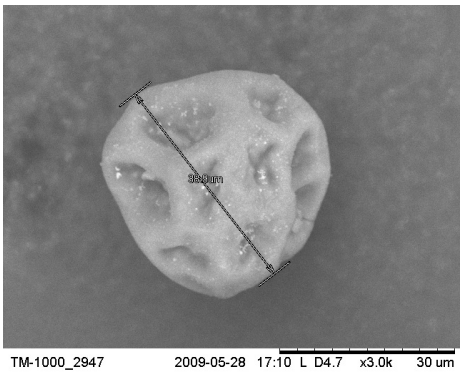
Element	Weight %
Sodium	4.7
Silicon	2.3
Sulfur	79.8
Chlorine	13.2

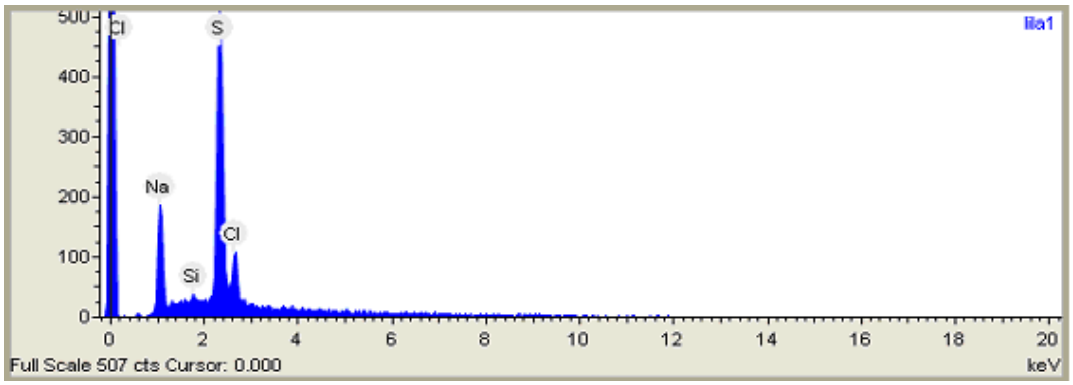
APPENDIX 9

Results from SEM analyses of purple dyestuff.

A)







Acquisition conditions

Acquisition time (s)	60.0
Process time	4
Accelerating voltage (kV)	15.0

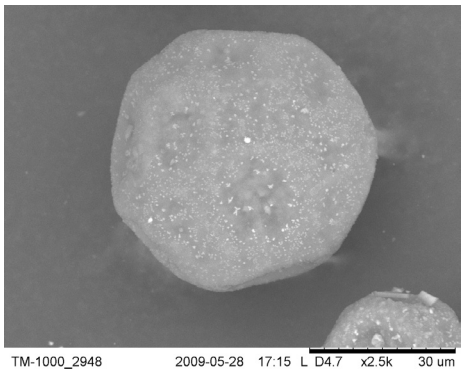
Quantification Settings

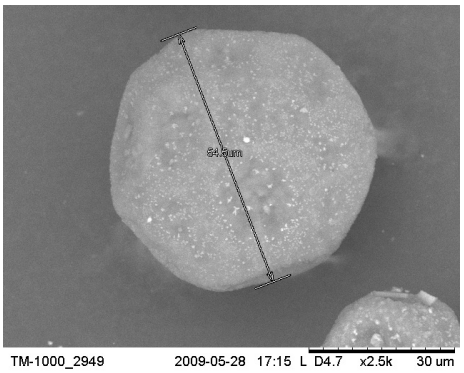
Quantification method	All elements (normalised)

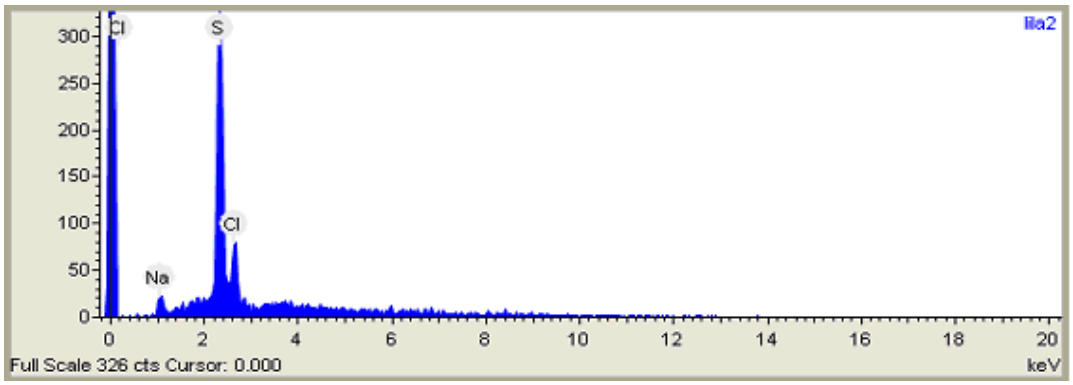
Summary results

Element	Weight %
Sodium	29.0
Silicon	0.9
Sulfur	54.9
Chlorine	15.2

B)







Acquisition conditions

Acquisition time (s)	60.0
Process time	4
Accelerating voltage (kV)	15.0

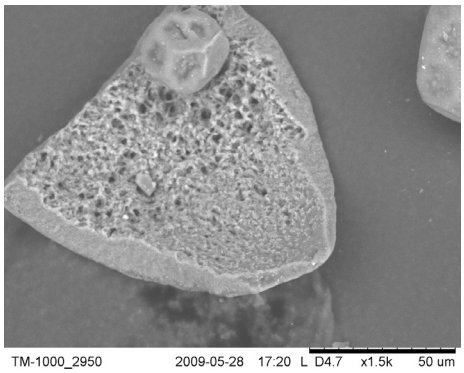
Quantification Settings

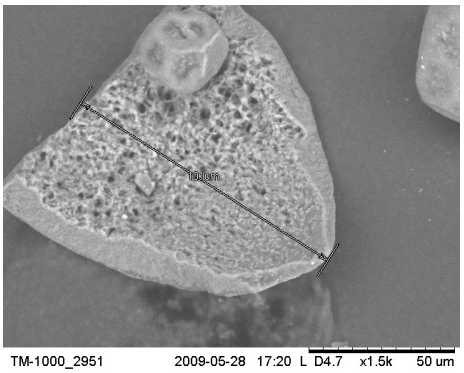
Quantification method	All elements (normalised)

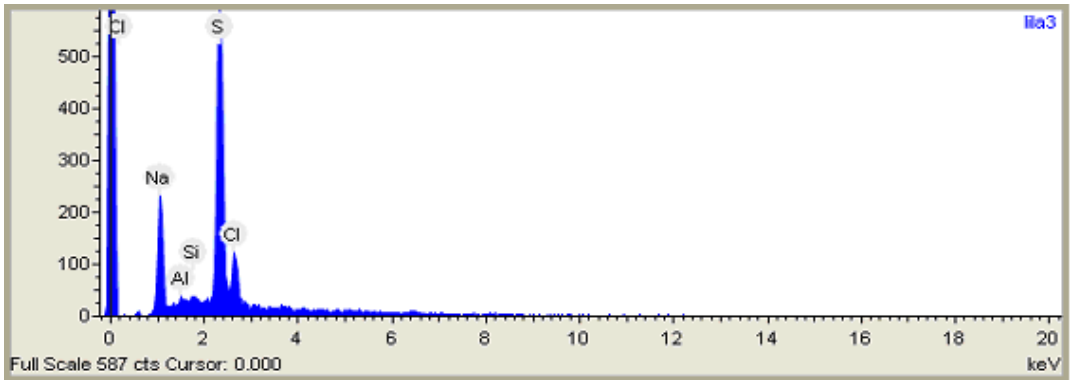
Summary results

Element	Weight %
Sodium	8.2
Sulfur	68.4
Chlorine	23.4

C)







Acquisition conditions

Acquisition time (s)	60.0
Process time	4
Accelerating voltage (kV)	15.0

Quantification Settings

Quantification method	All elements (normalised)

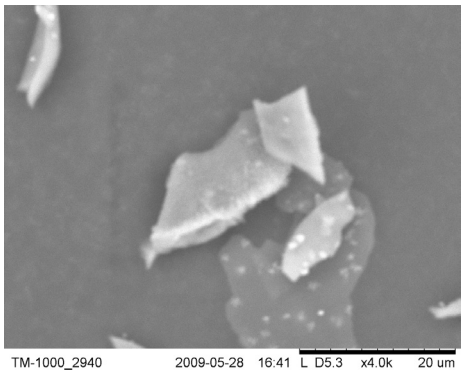
Summary results

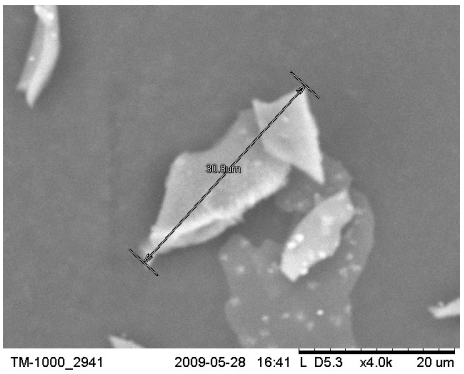
Element	Weight %
Sodium	30.2
Aluminum	0.8
Silicon	0.8
Sulfur	53.9
Chlorine	14.2

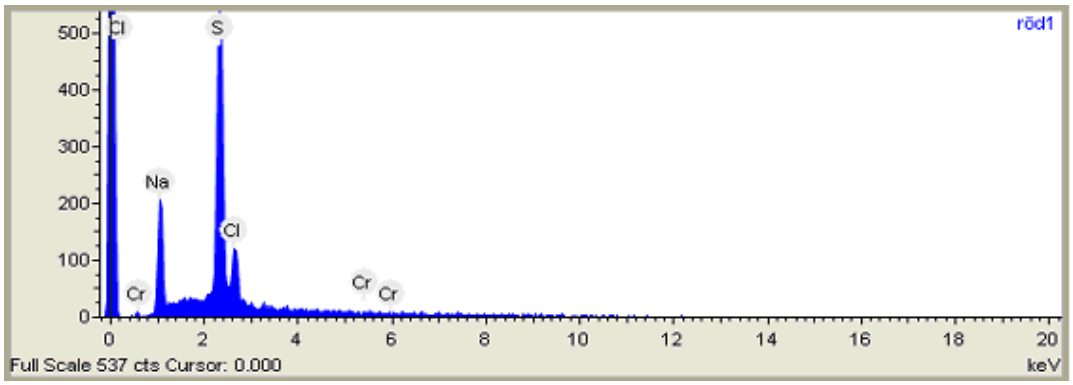
APPENDIX 10

Results from SEM analyses of red dyestuff.

A)







Acquisition conditions

Acquisition time (s)	60.0
Process time	4
Accelerating voltage (kV)	15.0

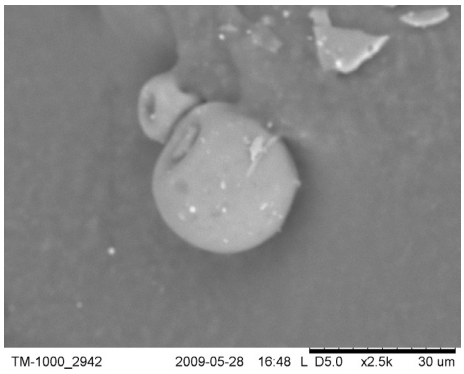
Quantification Settings

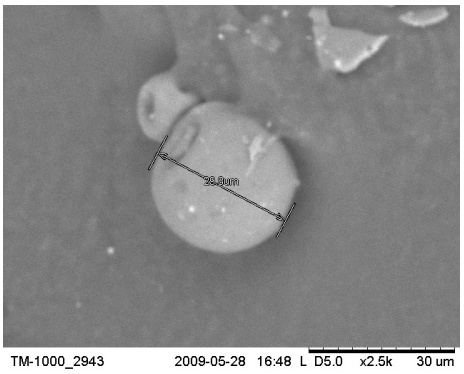
Quantification method	All elements (normalised)

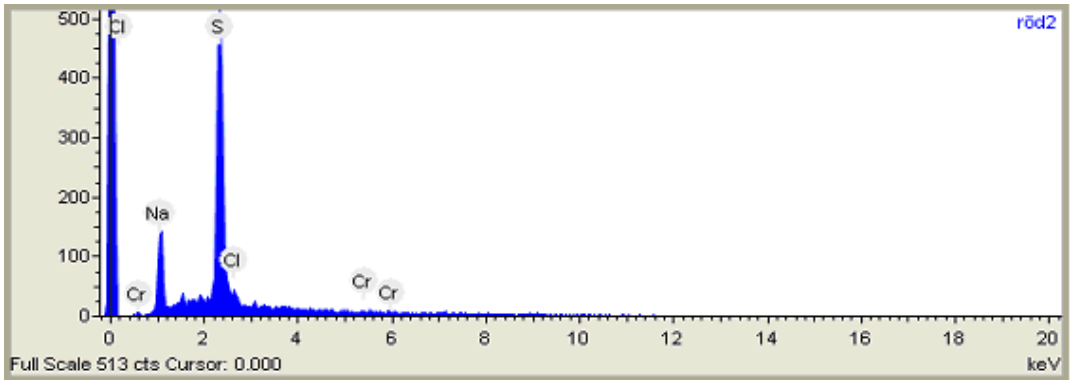
Summary results

Element	Weight %
Sodium	29.9
Sulfur	54.1
Chlorine	15.9
Chromium	0.1

B)







Acquisition conditions

Acquisition time (s)	60.0
Process time	4
Accelerating voltage (kV)	15.0

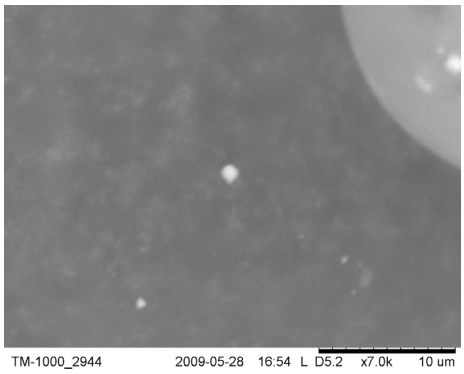
Quantification Settings

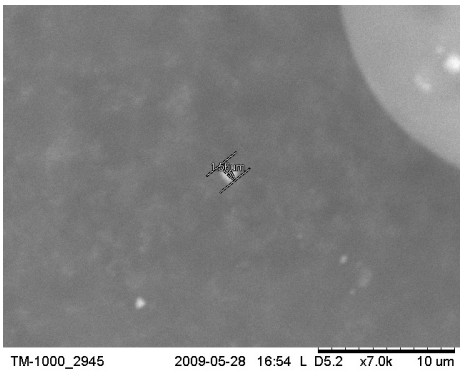
Quantification method	All elements (normalised)

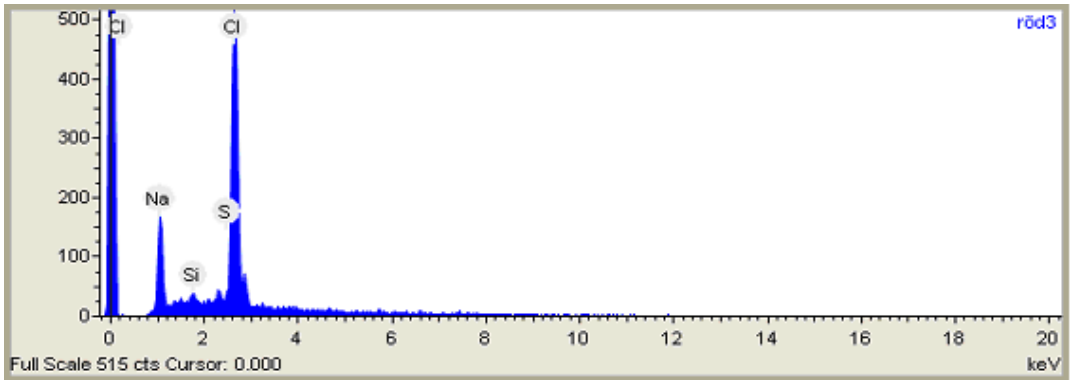
Summary results

Element	Weight %
Sodium	26.5
Sulfur	67.4
Chlorine	6.2
Chromium	0.0

C)







Acquisition conditions

Acquisition time (s)	60.0
Process time	4
Accelerating voltage (kV)	15.0

Quantification Settings

Quantification method	All elements (normalised)

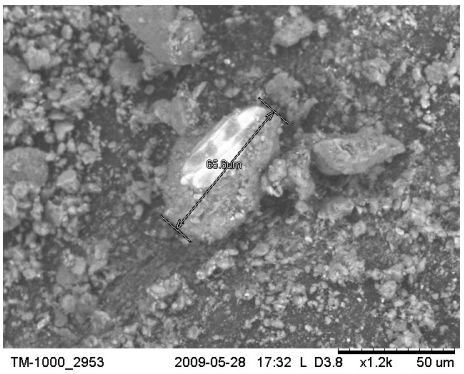
Summary results

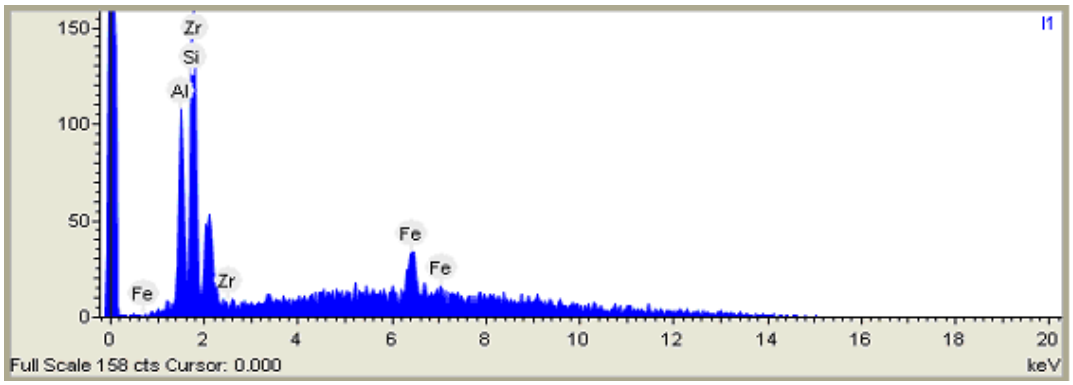
Element	Weight %
Sodium	29.2
Silicon	1.5
Sulfur	2.2
Chlorine	67.1

APPENDIX 11

Results from SEM analyses of laterite powder.

A)





Acquisition conditions

Acquisition time (s)	60.0
Process time	4
Accelerating voltage (kV)	15.0

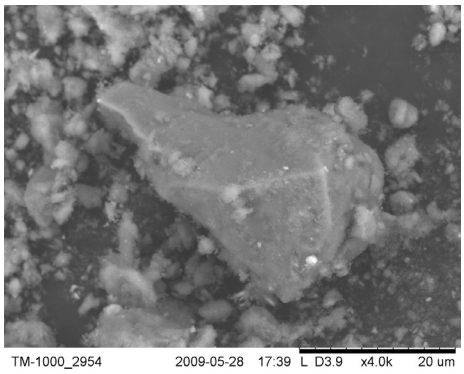
Quantification Settings

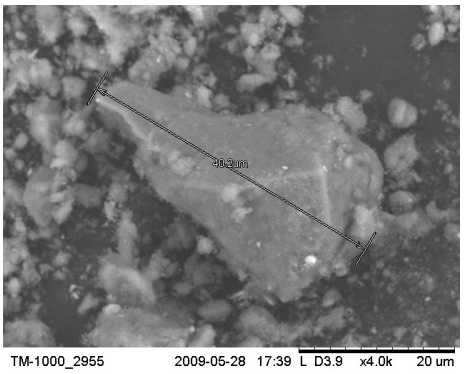
Quantification method	All elements (normalised)

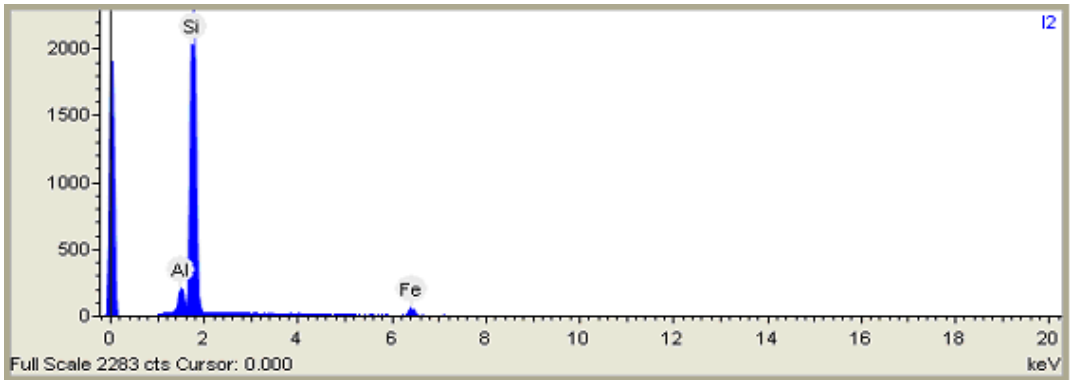
Summary results

Element	Weight %
Aluminum	17.2
Silicon	31.4
Iron	24.2
Zirconium	27.3

B)







Acquisition conditions

Acquisition time (s)	60.0
Process time	4
Accelerating voltage (kV)	15.0

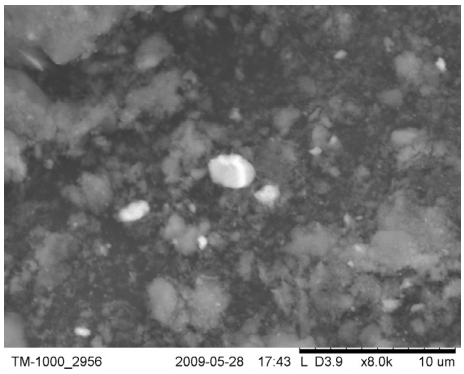
Quantification Settings

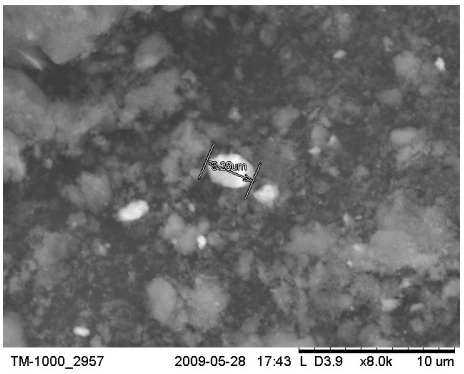
Quantification method	All elements (normalised)

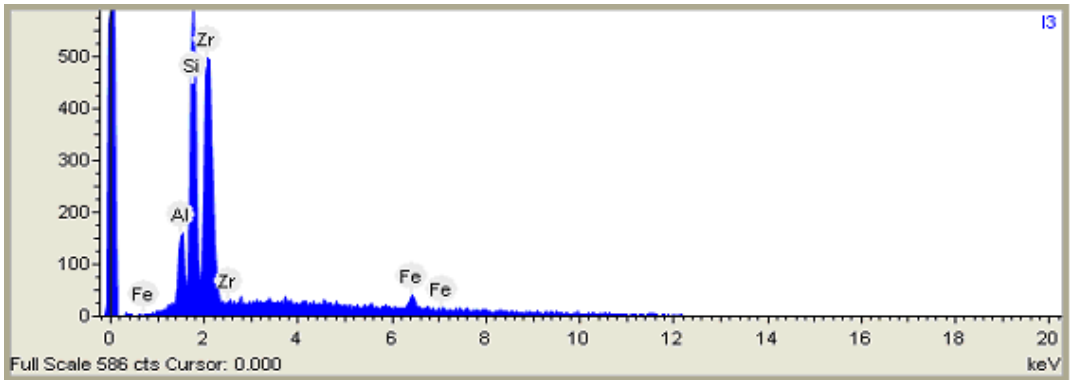
Summary results

Element	Weight %
Aluminum	5.8
Silicon	82.2
Iron	12.0

C)







Acquisition conditions

Acquisition time (s)	60.0
Process time	4
Accelerating voltage (kV)	15.0

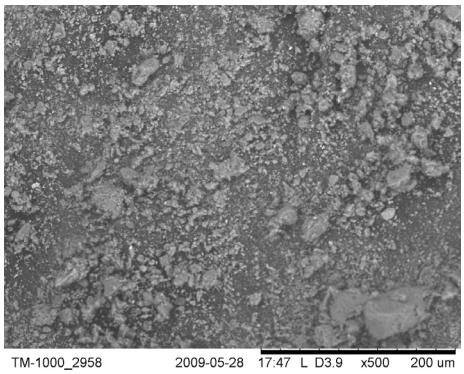
Quantification Settings

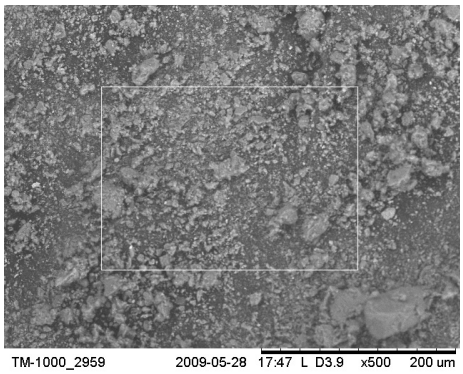
Quantification method	All elements (normalised)

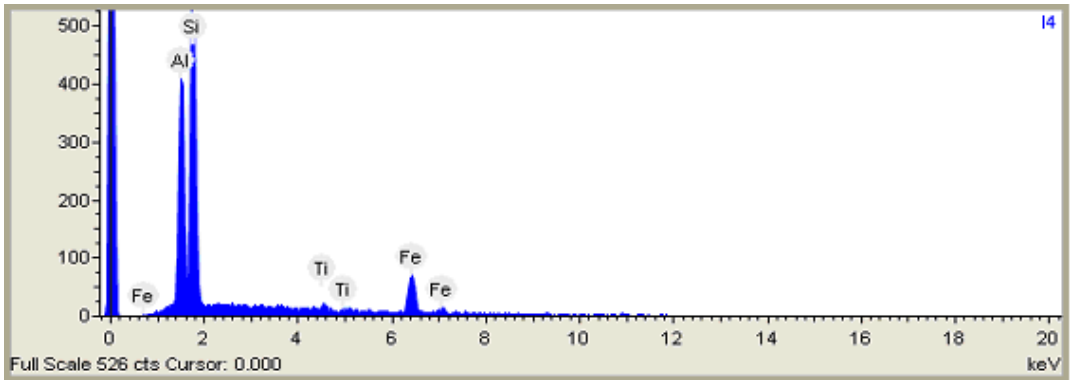
Summary results

Element	Weight %
Aluminum	6.1
Silicon	23.8
Iron	6.4
Zirconium	63.6

D)







Acquisition conditions

Acquisition time (s)	60.0
Process time	4
Accelerating voltage (kV)	15.0

Quantification Settings

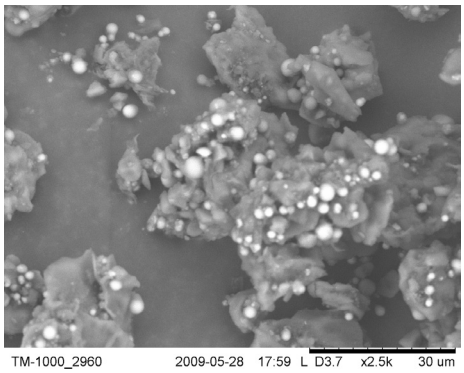
Quantification method	All elements (normalised)

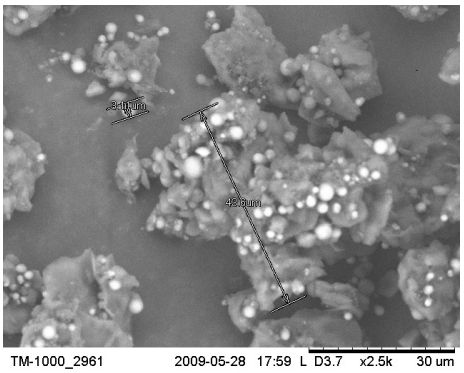
Summary results

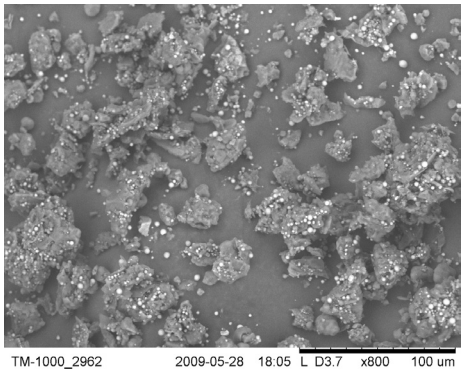
Element	Weight %
Aluminum	28.2
Silicon	43.6
Titanium	1.9
Iron	26.3

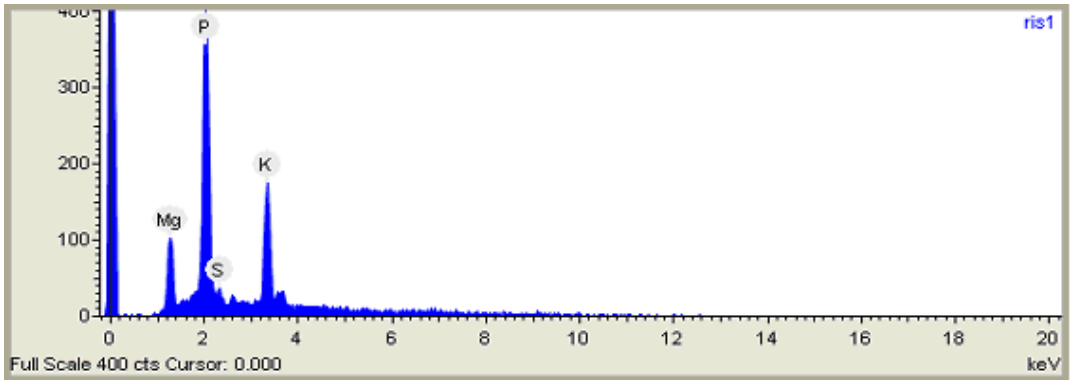
APPENDIX 12

Results from SEM analysis of rice bran powder.









Acquisition conditions

Acquisition time (s)	60.0
Process time	4
Accelerating voltage (kV)	15.0

Quantification Settings

Quantification method	All elements (normalised)

Summary results

Element	Weight %
Magnesium	13.3
Phosphorus	51.8
Sulfur	2.9
Potassium	32.1